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**Homogeneous Nucleation: A Problem in
Nonequilibrium Quantum Statistical Mechanics**

University of California

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Homogeneous Nucleation: A Problem in Nonequilibrium Quantum Statistical Mechanics

Alvin Richard Larson

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HOMOGENEOUS NUCLEATION: A PROBLEM IN NONEQUILIBRIUM QUANTUM STATISTICAL MECHANICS

by

Alvin Richard Larson

ABSTRACT

The master equation for cluster growth and evaporation is derived from many-body quantum mechanics and from a modified version of quantum damping theory used in laser physics. For application to nucleation theory, the quantum damping theory has been generalized to include system and reservoir states that are not separate entities. Formulae for rate constants are obtained. Solutions of the master equation yield equations of state and system-averaged quantities recognized as thermodynamic variables. Formulae for Helmholtz free energies of clusters in a Debye approximation are derived. Coexistence-line equations for pressure, volume, and number of clusters are obtained from equations-of-state analysis. Coexistence-line and surface-tension data are used to obtain values of parameters for the Debye approximation. These data are employed in calculating both the nucleation current in diffusion cloud chamber experiments and the onset of condensation in expansion nozzle experiments. Theoretical and experimental results are similar for both cloud chamber and nozzle experiments, which measure water. Comparison with other theories reveals that classical theory only accidentally agrees with experiment and that the Helmholtz free-energy formula used in the Lothe-Pound theory is incomplete.

CHAPTER 1

INTRODUCTION

Homogeneous nucleation, a field of chemical physics, is concerned with predicting the rate of droplet formation in a supersaturated vapor free of foreign nuclei or ions that may serve as condensation sites. The subject of nucleation has been studied extensively over the past fifty years by many researchers. A comprehensive review is given by Dunning (1969), and a book about homogeneous nucleation has been written by Abraham (1974). We will emphasize, in our introductory review, only the most important developments in basic theory and some of the experimental results that affect the validity of theoretical findings. We will briefly review the experimental devices used for the study of nucleation, then the theoretical development, and finally the results of our work.

Several experimental devices are used to study the nucleation process. The oldest is the expansion cloud chamber invented by Wilson (1897) and reviewed by Feder et al (1966). Analytic equations for supersonic nozzle flow with condensation were developed by Oswatitsch (1942), and the expansion nozzle was developed into a useful tool for condensation studies by Wegener (1954, 1964, 1970, 1972) and coworkers. Very high supersaturation ratios can be obtained with an expansion nozzle. Langsdorf (1939) invented the diffusion cloud chamber and Franck and Hertz (1956) constructed the first upward diffusion cloud chamber, the type currently used in nucleation studies. Use of the diffusion cloud chamber for nucleation studies is described by Katz and Ostermeier (1967). Results from diffusion cloud chamber experiments are

directly comparable with theoretical calculations of droplet formation rates. Free jets [Golomb et al (1972)] and shock tubes [Barschdorff (1975)] have been used recently as tools for nucleation studies.

The first homogeneous nucleation theory was developed by Volmer and Weber (1926). They noted that Gibbs (1875) has proven that, in a super-saturated vapor, droplets containing an energy

$$F_{\Gamma} = \frac{1}{3} W_{\Gamma} \gamma \quad (1-1)$$

are metastable. In the preceding equation W_{Γ} is the area of the metastable (critical size) droplet (cluster) containing Γ molecules and γ is the surface tension. Volmer and Weber (1926) also deduced, from Einstein (1910), that the probability of existence of a metastable droplet of Γ molecules is

$$P_{\Gamma} = e^{-F_{\Gamma}/kT}, \quad (1-2)$$

where k is Boltzmann's constant and T is the temperature. They concluded, in analogy with Arrhenius' (1889) equations for chemical kinetics, that J , the frequency of droplet formation by fluctuations, is proportional to P_{Γ} , i.e.,

$$J = C_{vw} e^{-W_{\Gamma}\gamma/3kT}, \quad (1-3)$$

where C_{vw} is a proportionality factor that may be a slowly varying function of droplet size. To find the area of the metastable droplet, Volmer and Weber (1926) employed the Thomson (Lord Kelvin) (1870) equation,

$$kT \ln \frac{P}{P_s} = \frac{2 m \gamma}{\rho R_{\Gamma}}, \quad (1-4)$$

where P is the vapor pressure, P_s is the saturation vapor pressure, m is the mass of a molecule, ρ is the liquid density, and R_{Γ} is the radius

of the critical-size droplet. Equation (1-4) is usually called the Gibbs-Thomson equation. Volmer and Weber (1926) presented a table of water cluster sizes as a function of supersaturation ratio, P/P_s , to demonstrate that the nucleation current, J , is very sensitive to the supersaturation ratio. Their paper established two long-standing notions about nucleation: (1) that the nucleation current is controlled by critical-size clusters, and (2) that the growth from monomers, dimers, etc. to critical-size clusters occurs through number fluctuations in the system.

Farkas (1927) introduced improvements that resulted in partial evaluation of the preexponential factor, C_{vw} , of Volmer and Weber (1926); but his result also contained an unknown factor. He was the first to introduce an expression for the steady-state rate of droplet formation per unit volume (nucleation current):

$$J = a P W_\alpha \bar{Z}_\alpha - a P_{\alpha+1} W_{\alpha+1} \bar{Z}_{\alpha+1} \quad (1-5)$$

where a is a proportionality factor, $\bar{Z}_\alpha$ is the number density of clusters containing α molecules, and P_α is the internal pressure of a cluster of α molecules. Farkas (1927) also introduced kinetic theory in calculating the cluster growth rate per unit area, i.e., he set

$$aP = \frac{P}{\sqrt{2\pi m^* kT}} \quad (1-6)$$

Farkas (1927) obtains a pseudosteady-state distribution of cluster size, $Z_\alpha(ps)$, by using the Gibbs-Thomson equation, Eq. (1-4), and a pseudoequilibrium condition. The pseudoequilibrium condition is defined by $J = 0$ and by a specific monomer density that is implied by a given pressure, P . We make the definition to distinguish this distribution both from a

true equilibrium and a true steady-state distribution. The condition $J = 0$ can only occur when the system is in complete particle equilibrium, in which case the monomer density is not an independent variable, but is an implicit function of the number of molecules, of volume, and of temperature. The pseudosteady-state distribution implies that there is an infinite number of infinite-size clusters. To restore physical reality, later researchers [McDonald (1963)] introduced a Maxwell's demon to reflect molecules evaporated from large clusters back into the vapor. Use of the pseudoequilibrium condition is often referred to in later work as the application of detailed balance. Farkas (1927) uses Z_1 (ps) to obtain the following result for the steady-state nucleation current:

$$J = \frac{P}{\rho kT} \sqrt{\frac{2 m \gamma}{\pi}} \left\{ \frac{C_f}{W_r} \right\} e^{-W_r \gamma / 3kT} \quad (1-7)$$

where C_f is the unknown proportionality factor.

Becker and Döring (1935) derived the first nucleation-current equation claimed to be free from any unknown proportionality factor. Their result is approximately (within a factor of ten) equal to the current predicted by the nucleation theory commonly referred to as "classical". We consider a factor-of-ten error in nucleation current small because small variations in the argument of the exponential will cause currents to vary over many orders of magnitude. From formulae in their paper, we write the Becker-Döring (1935) result in the following form for comparison with other theories:

$$J = \frac{P}{\rho kT} \sqrt{\frac{2 m \gamma}{\pi}} \left\{ \frac{4\sqrt{3} Z_1(\text{ps})}{r^{2/3}} \right\} e^{-W_r \gamma / 3kT} \quad (1-8)$$

Becker and Döring (1935) use their theory to calculate a critical supersaturation pressure and compare their result with expansion cloud chamber measurements (for water) by Volmer and Flood (1934). Theory and experiment were in close agreement, indicating that the Volmer and Weber (1926) theory had been "normalized". However, this agreement is now considered fortuitous; Kuhrt (1952b), Feder et al (1966), and Dunning (1969) criticize the Becker-Döring theory because the assumption that the Gibbs-Thomson equation is valid for dimers, trimer, etc., cannot be justified. The factor $Z_1(ps)$ is actually unknown because it is determined by the starting point of a summation and the value of the summation is insensitive to the starting point [see the equation between Eq. (9a) and Eq. (10) of the Becker and Döring (1935) paper].

Early nucleation theory was concerned only with irreversible condensation and relied on measured pressure along the coexistence line for part of the input data. Mayer (1937) and Mayer and Ackerman (1937) were the first to study the related problem of reversible condensation, i.e., they calculated the pressure and cluster distributions (including conditions along the coexistence line) of a system in particle equilibrium. Their development is based on the canonical ensemble of classical statistical mechanics and mathematical definition of clusters based on the proximity of molecules. They derived equations for pressure P_s and specific volume v_s along the coexistence line and obtained qualitative agreement with experimental results. A different approach, based on a dissociation theory developed by Fowler (1936), was presented by Band (1939a). Fowler (1936, Sec. 9.6) observed that an imperfect gas can be treated as a problem in dissociation and that the law of mass action

(which he derived) describes the amount of dissociation in equilibrium. The law of mass action as given by Band (1939a) is

$$\bar{n}_\alpha(\text{eq}) = \left[\frac{\bar{n}_1(\text{eq})}{Q_1(T)} \right]^\alpha Q_\alpha(T) \quad , \quad (1-9)$$

where $Q_\alpha(T)$ is the canonical partition function (representing translational, rotational, and vibrational free energies) for clusters of α molecules and $\bar{n}_\alpha(\text{eq})$ is the equilibrium number of clusters of α molecules in a particular example of the assembly. The pressure is calculated from the perfect gas law:

$$P = \frac{kT}{V} \sum_\alpha \bar{n}_\alpha(\text{eq}) = kT \frac{N}{V} \quad , \quad (1-10)$$

where N is the number of clusters and V is the volume. Band (1939a) proved that, except for excluded volume effects [Band (1939b)], Mayer's (1937) cluster theory is a special case of Fowler's dissociation theory. He also introduced a cluster partition function:

$$Q_\alpha(T) = \frac{V}{\lambda^3(\alpha)} e^{-[(\alpha-1)I + \chi(\alpha,T)]/kT} \quad , \quad (1-11)$$

where $\lambda(\alpha)$ is the usual thermal wavelength for a cluster of α molecules representing translational free energy, I is a constant internal energy, and $\chi(\alpha,T)$ is a surface energy. By using this partition function and the law of mass action, Band (1939a) constructed coexistence line equations (for P_s , V_s , and $N = P_s V_s / kT$) that are functions of surface tension only. The results were compared with experiment by Tseng, Feng, Cheng,

and Band (1940) and were found to be qualitatively correct (as the Mayer theory was). The quantity,

$$\frac{\bar{n}_1(\text{eq})}{Q_1(T)} = e^{\mu/kT}, \quad (1-12)$$

can be identified as an activity where μ is a chemical potential. According to the law of mass action, the distribution function from Eqs. (1-9) and (1-12) is:

$$\bar{n}_\alpha(\text{eq}) = Q_\alpha(T) e^{\alpha\mu/kT}. \quad (1-13)$$

In the same year that Band published his dissociation cluster theory, Frenkel (1939) derived another equilibrium distribution function,

$$N_\alpha(\text{eq}) = N \exp \left[- [(\phi_g - \phi_\ell) \alpha + C_\gamma \alpha^{2/3}] / kT \right], \quad (1-14)$$

where ϕ_g and ϕ_ℓ are thermodynamic potentials for the gas and liquid phases, respectively, and C_γ is a coefficient related to the surface tension. To derive Eq. (1-14), Frenkel minimized a mixed-phase potential. The factor N is introduced by an assumed entropy term in the thermodynamic potential. The assumed entropy is based on cluster fractions rather than on the more correct distribution of energy levels [see Fetter and Walecka (1971, p.49) or Eq. (4-44) (with $\bar{n}_{i\alpha} \ll 1$) of this work]. Comparison of Eqs. (1-11) and (1-13) with Eq. (1-14) reveals the similarities and differences between Band's distribution and Frenkel's. The quantity $(\alpha-1)I - \alpha\mu$ in Band's distribution corresponds to $(\phi_g - \phi_\ell)\alpha$ in Frenkel's distribution and $\chi(\alpha, T)$ corresponds to $C_\gamma \alpha^{2/3}$. Neither

distribution considers rotational free energy (although rotation could conceivably be included in Band's internal energy, I) and Frenkel's distribution contains an extra factor N , and no translational free energy.

Further developments pertaining to nucleation current were made by Zel'dovich (1942) who introduced the first complete monomer-controlled master equation. It consists of a forward and backward current, both of the Farkas (1927) type, i.e.,

$$\frac{dz_{\alpha}}{dt} = - z_{\alpha} [q_{+}(\alpha) + q_{-}(\alpha)] + z_{\alpha-1} q_{+}(\alpha-1) + z_{\alpha+1} q_{-}(\alpha+1) \quad , \quad (1-15)$$

where $q_{+}(\alpha)$ is the growth rate for clusters of α molecules by monomer accretion and $q_{-}(\alpha)$ is the monomer evaporation rate from clusters of α molecules. Similar to Farkas (1927), Zel'dovich (1942) used a pseudo-equilibrium detailed balance condition to relate growth rates to evaporation rates in terms of a pseudosteady state distribution. He assumed that the pseudosteady-state distribution has the form

$$z_{\alpha}(ps) = e^{-\phi(\alpha)/kT} \quad , \quad (1-16)$$

determines an approximate solution of the differential equation by the method of steepest descent, and obtains the steady-state current

$$J = q_{+}(\Gamma) z_{\Gamma}(ps) \left[- \frac{1}{2\pi kT} \frac{d^2\phi(\alpha)}{d\alpha^2} \bigg|_{\alpha=\Gamma} \right]^{1/2} \quad . \quad (1-17)$$

Frenkel (1946, p. 382) claims that a distribution function of the type given by Eq. (1-13) is the result of a "rough" thermodynamic treatment and that the distribution of embryos is given by the "more general" distribution, Eq. (1-14). Furthermore, Frenkel (1946, p. 391) implies

that the pseudosteady-state distribution required for Zel'dovich's (1942) theory, Eq. (1-16), is the equilibrium distribution from Eq. (1-14) with N/V replaced by $Z_1(\text{ps})$. Frenkel (1946, p. 391) also uses kinetic theory, as Farkas (1927) did, to find q_1 . The nucleation current derived by Frenkel (1946) using Zel'dovich's results, Eq. (1-17), can be written

$$J = \frac{P}{\Omega kT} \sqrt{\frac{2m\gamma}{\pi}} \left\{ Z_1(\text{ps}) \right\} e^{-W_F\gamma/3kT} \quad (1-18)$$

The preceding equation, which represents classical nucleation theory, was also derived by McDonald (1962, 1963).

Classical nucleation theory uses the infinite-medium surface tension to calculate the surface energy of critical-size clusters, which may be smaller than 100 molecules, with no correction for variations in surface tension with cluster size. This approximation is called the capillarity approximation. Tolman (1949) developed an equation for the surface tension of a droplet as a function of cluster size,

$$\gamma(R) = \gamma(\infty) \left(1 + \frac{2\delta}{R} \right)^{-1}, \quad (1-19)$$

where δ is a constant of the order of one molecular radius. This equation, confirmed by Kirkwood (1949), provided the basis for later doubts [Pound (1952)] about the validity of the capillarity approximation and, consequently, about classical and other nucleation theories that use it.

The dissociation model of Band (1939a) was employed in an alternative nucleation theory developed by Kuhrt (1952a, 1952b). Kuhrt's model includes cluster translational and rotational effects and accounts for the resultant missing six degrees of freedom in the internal (vibra-

tional) energy. His result, however, is a current with the same p^2 dependence in the pre-exponential factor as the classical theory, Eq. (1-18). It was later noted by Feder et al (1966) that Kuhrt (1952b) erroneously evaluated the deactivation term.

Bolstered by its success in predicting critical supersaturation ratios for expansion (Wilson) cloud chamber experiments by Volmer and Flood (1934) [see Abraham (1974, table 5.2)], classical nucleation theory became the accepted theory. For about fifteen years following Frenkel's (1946) book, most of the publications were either concerned with minor refinements to the classical theory or with expressions of doubt about its validity. The analytic methods for adapting classical (Becker-Döring) nucleation theory to nozzle flow were developed by Oswatitsch (1942). Stever (1950) reported that experimental measurements in hypersonic wind tunnels indicate that supersaturation ratios can be much higher than predicted by classical nucleation theory. He also noted that in classical nucleation theory, temperature variation of the surface tension is accounted for, but droplet size is not; a modified theory that accounts for cluster size variation of surface tension predicts higher supersaturation ratios. Probstein (1951) also noted disagreement between theory and experiment in supersonic wind tunnel measurements by Head (1949) and by Wegner and Smelt (1950). Probstein (1951) and Kantrowitz (1951) investigated the possibility of a delay time (in establishing a steady-state current) causing the discrepancy. They and other researchers [Collins (1955), Wakeshima (1954), Feder et al (1966), Andres (1965)] report that delay times are much shorter than times required for a gas to traverse a nozzle and hence must have negligible effect. The delay time studies are summarized by Abraham (1974,

p. 101). At the Christmas Chemical Engineering Symposium in 1952, LaMer (1952) and Pound (1952) noted that the agreement between classical theory and its predictions is much better than justified by theoretical uncertainties; and Reiss (1952) notes that classical nucleation theory is based on semiphenomenological and quasi-thermodynamic arguments and should be replaced by the dynamical analog of the Mayer cluster theory. At this same conference, Langsdorf (1952) suggested that the diffusion cloud chamber be used as a tool for nucleation studies.

The theory of reversible condensation was further advanced by Yang and Lee (1952). They analyzed the grand partition function by allowing complex values for fugacity and found that a study of phase transitions could be reduced to an investigation of the roots of the grand partition function. They found Mayer's theory not applicable to the liquid phase because cluster integrals were replaced by their limiting values. The analysis of Yang and Lee (1952) was very general, i.e., the interaction between particles is written in very general terms; however, it established the fact that the physics required to describe phase changes (in an equilibrium system) is contained in the grand partition function and that the details of the phase change will depend on the particular partition function used, i.e., on Helmholtz free energy.

Courtney (1962) derived an equation that describes the steady-state nucleation current in terms of saturation ratio and an equilibrium distribution of clusters per unit volume. The saturation ratio is defined as

$$S = \frac{Z_1(ss)}{Z_1(eq)} \equiv \frac{\bar{n}_1(ss)}{\bar{n}_1(eq)} \quad , \quad (1-20)$$

where $Z_1(ss)$ is the steady-state number density of monomers and $Z_1(eq)$ is the equilibrium number density of monomers. Courtney (1962) writes the rate constant in Zel'dovich's master equation, Eq. (1-15), in the following form:

$$q_+(\alpha) = k_\alpha Z_1(eq) S \quad (1-21)$$

He uses Eq. (1-15), Eq. (1-21), and the law of mass action to obtain the following equation for the nucleation current:

$$J = \left[\sum_{\alpha=1}^{\Omega} \frac{1}{k_\alpha Z_1(eq) S^{\alpha+1} Z_\alpha(eq)} \right]^{-1} \quad (1-22)$$

Courtney (1962) terminates the sum at an undetermined cluster size Ω ; however, Ω can be infinity if the distribution of clusters is in a proper form that allows convergence of the sum. The sum in Eq. (1-22) can be evaluated by the method of steepest descent to obtain an equation similar to Eq. (1-17), valid if the critical cluster size is not too small. Equation (1-22) draws attention to the need for further development of the equilibrium distribution function from the law of mass action, Eq. (1-13), and places the work of Band (1939a) and Yang and Lee (1952) into perspective. If we assume that

$$Z_\alpha(eq) S^\alpha = Z_\alpha(ps) \quad (1-23)$$

and if we substitute Eqs. (1-23) and (1-21) into Eq. (1-22), we obtain the nucleation current equation derived by McDonald (1962). The McDonald (1962) result was obtained from detailed balance and a pseudoequilibrium condition [as Farkas (1927) did]. However, the derivation of Eq. (1-22)

was not the primary objective of Courtney's work; hence, it remained unnoticed and the pseudosteady-state distribution continues to be used in nucleation theory [see Burton (1977)]. Both derivations yield the same nucleation current; however, the pseudosteady-state concept does not have an adequate theoretical basis.

The ideas of Band (1939) and Kuhrt (1952) failed to influence the development of nucleation theory and it was through an independent work of Lothe and Pound (1962) that they reappeared. Lothe and Pound (1962) noticed that the classical theory did not follow the laws of statistical mechanics; the factor $Z_1(ps)$ [in Eq. (1-18)] does not belong there and, additionally, the free energy of critical-size clusters must be amended to account for (1) translational energy states, (2) rotational energy states, and (3) the six degrees of freedom missing from the liquid-drop internal energy because they are taken by translational and rotational states. Inclusion of these factors increases the classical nucleation current by 17 orders of magnitude. They concluded that agreement between classical theory and experiments must be fortuitous and postulated that a thermal nonaccommodation factor would account for the large discrepancy; however, the work of Feder, Russel, Lothe, and Pound (1966) shows that this assumption is not true. Feder et al (1966) also found that a 15% increase in surface tension would restore agreement between Lothe-Pound theory and expansion cloud chamber experiments for water and that a decrease in the preexponential factor by a factor of 10^{-15} would also give agreement. Such a large preexponential factor could not be accounted for by an accommodation coefficient. Hirth and Pound (1963) reported that an accommodation coefficient of 1.0 is common among materials with large binding energy unless the temperature is very high.

The work of Lothe and Pound (1962) became known as the Lothe-Pound theory and caused considerable controversy in the literature. Riess and Katz (1967) claimed that the classical theory did not neglect translational and rotational free energy of critical-size clusters, but their arguments were refuted by Abraham and Pound (1968). Riess, Katz, and Cohen (1968) repeated the claim. They rightfully argue that rotation is not considered in the potential part of the Hamiltonian, but they apparently did not notice that rotation about the center of mass is included in the momentum part of the Hamiltonian. Kikuchi (1969) used a lattice gas model to refute the Lothe-Pound theory; however, the lattice gas model is believed to be unrealistic [Kiang et al (1974)]. Derjaguin (1972) relied on intuitive statistical mechanics and on an apparently unjustified normalization to rederive the classical nucleation current.

Experimental measurements have not been able to prove conclusively which theory (if any) is correct. Abraham (1968a) observed that the behavior of some materials is described by classical theory and of some by Lothe-Pound theory. The Lothe-Pound theory was most successful in nozzle experiments [see Jaeger et al (1969) and Dawson et al (1969)]; however, Katz et al (1976) have completed diffusion cloud chamber experiments with materials that had been well-described by Lothe-Pound theory in nozzle experiments, and found that classical theory describes these experiments very well. Water is described well by classical theory in both nozzle [Jaeger et al (1969)] and diffusion cloud chamber experiments [Heist and Riess (1973)]. Burton (1977, Fig. 9) observed that classical theory generally gives good agreement with diffusion cloud chamber experiments, but that there is an apparent systematic difference as evidenced by a curve crossing in a supersaturation vs temperature graph for n-butylbenzene.

Following the Lothe-Pound (1962) theory, the next noteworthy theoretical development was by Fisher (1967). His theory is based on two assumptions: (1) interactions between clusters can be neglected and (2) the mean surface of a cluster has the expected properties and characterizes all cluster sizes sufficiently well. Fisher (1967) developed a generalized partition function (similar to a grand canonical partition function) from the liquid-drop model for free energy of clusters [such as the free energy represented by Eq. (1-11)]. The Fisher (1967) equation for the pressure is

$$P = kT q_0 \sum_{\alpha=1}^{\infty} \alpha^{-\tau} (x^{\alpha})^{\sigma} y^{\alpha} , \quad (1-24)$$

where q_0 is a constant, τ and σ are parameters, y is proportional to the activity, and the term $(x^{\alpha})^{\sigma}$ is related to the surface tension with x a measure of temperature. Fisher (1967) uses his partition function to show that an essential singularity exists representing a phase transition and that above a critical temperature a phase transition does not exist. The "derby hat" behavior near the critical point on a p - v diagram predicted by Mayer theory does not exist in the Fisher (1967) equation of state. The Fisher (1967) result, which has become known as the Fisher droplet model, has received further theoretical development from Eggington et al (1971), Kiang et al (1971), Kiang et al (1974), and Hamill et al (1974). Kiang et al (1971) note that all previous nucleation theories are special cases of the Fisher droplet model. By using the same basic idea as Tseng et al (1940) and Abraham (1968b), but a different technique, Kiang et al (1971) use the Fisher coexistence line equation and corresponding data for water to find parameters for an effective surface

tension. The parameters are used to calculate diffusion cloud chamber measurements and agreement between theory and experiment is found.

Kiang et al (1974) applied the same technique to other materials and found improved agreement over classical theory.

Buckle (1969) pioneered attempts to formulate nucleation theory from molecular rather than from thermodynamic precepts. Burton (1970) used an energy minimization procedure and a Leonard-Jones potential to study small clusters of argon. He observed that in small clusters: atoms are farther apart than in the bulk; surface, transverse, and longitudinal modes of vibration exist; and the heat capacity is quite different from that for an infinite medium. McGinty (1971) used similar relaxation techniques to discover that the free energy of clusters has the same qualitative behavior as predicted by the liquid-drop model but that this method is not practical for most nucleation calculations because the technique is only applicable at very low temperatures. In a following paper, McGinty (1972) also used relaxation techniques to discover that if a cluster contains several stable configurations, they should all be included in the calculation of the free energy; but if the most stable configuration is found, it is not necessary to include any others. One configuration can be the most stable at one temperature and another at a different temperature. Burton (1973) used results of small-cluster calculations of Helmholtz free energy (including rotation and translation) to compute a universal set of curves that give a correction factor for the supersaturation ratio predicted by classical theory as a function of reduced temperature. Application of the curves to several classical calculations of supersaturation ratio for several different materials and temperature conditions shows a remarkable

improvement in agreement between theoretical and experimental results. Burton (1973) believes that the long-standing controversy about the necessity of rotational-translational corrections is resolved by this work and that the apparent discrepancies between Lothe-Pound theory and experiments reflects the need for consideration of corrections besides rotation and translation. Other small-cluster calculations were made by Hale and Plummer (1974) who studied ice, Hoar and Pal (1975) who found that the specific heat of larger argon clusters obeys a T^3 law at low temperature, and Briant and Burton (1975) who used a molecular dynamics technique to study water. Kaelberer and Etters (1977) used a Monte Carlo technique and were able to observe liquid-to-solid phase changes in all cluster sizes. They noticed anharmonic effects and found that different cluster sizes have different melt temperatures. Miyazaki *et al* (1977) compared Monte Carlo calculations of small-cluster free energies with classical and Lothe-Pound free energies. Rusanov and Brodskaya (1977) used molecular dynamics techniques to study small drops of liquid. Their calculations of surface tension give qualitative agreement with Tolman's (1949) formula.

Questions concerning the proper definition of a cluster are discussed by Golden (1969, p. 116). He gives the advantages and disadvantages of configuration criteria and energy criteria for cluster definition. The Mayer (1937) theory could be classified as a configuration criterion; however, Gillis *et al* (1977a) observe that Mayer's cluster is not a physical cluster, but is a mathematical cluster representing several molecules in close proximity over a period of time much longer than a collision time. The fundamental dynamical entity in Mayer's theory is the individual molecule. Attempts, by Hill (1956, Ch. 5), at modification

of Mayer's theory to define the clusters physically led to the difficulty of having a small system partly defined by its momentum. Gillis et al (1977b) proved from a configuration criterion that the law of mass action is valid for finding the equilibrium distribution in a one-dimensional configuration analysis. The law of mass action is derived by an independent particle approximation; hence, the work of Gillis et al (1977b) partly answers the question of why interactions between clusters need not be included when calculating equilibrium distributions. This result is significant because the law of mass action plays a key role in nucleation theory.

Until 1970, the rate of cluster growth was determined by the assumed Zel'dovich master equation, Eq. (1-15); and because the master equation was assumed, it was necessary to rely on several other seemingly unrelated principles (detailed balance, equilibrium statistical mechanics, and kinetic theory) to obtain the rate constants. An early theory that circumvents the assumed master equation was developed by Strickfaden and Sobrino (1970) who solved the Boltzmann equation in the fluid dynamic approximation to obtain the time evolution of the density distribution about a single cluster. Bashkirov (1970) used an operator in cluster-size space and an ad hoc master equation for this operator to derive the Fokker-Planck equation previously derived from the assumed master equation by Zel'dovich (1942). Hagen and Kasner (1974) use a semi-phenomenological method that avoids detailed balance to calculate the rate constant for emission of a molecule from a water trimer. Lowry and Snider (1974) and Snider and Lowry (1974) developed a pair of coupled rate equations for dimer and trimer formation. They use projection operators (onto free and bound states) to generate superoperators

used extensively in the development. Expressions for rate constants for recombination and decompositions are found (without detailed balance) in terms of transition rates in accord with Fermi's golden rule.

In summary, it appears that a satisfactory nucleation theory does not yet exist. One theoretically bothersome problem in many derivations is the improper use of detailed balance (a principle applicable only in true equilibrium) in the steady state to relate the rate constants; however, this is compensated for by the use of a pseudosteady-state distribution function. The result is the same as that predicted by the theoretically consistent Courtney (1962) current, which expresses the current as a function of true-equilibrium distribution functions. Concentrating on problems with the equilibrium distribution function, we observe that homogeneous nucleation theories still have many inconsistencies. Classical theory gives excellent agreement with diffusion cloud chamber experiments and is recommended for engineering calculations by Gyarmathy (1976); yet it does not have a firm theoretical basis. In addition to the use of a distribution function that is different from the one predicted by statistical mechanics (or the law of mass action), as observed by Lothe and Pound (1962), classical theory uses bulk surface tension to calculate the free energy of clusters that may contain only a few tens of molecules. The Lothe-Pound theory predicts nucleation currents 17 orders of magnitude greater than predicted by classical theory; hence, its results are in very poor agreement with diffusion cloud chamber experiments. Concerning the use of bulk surface tension, Lothe-Pound theory is also open to the same criticism as classical theory. The Lothe-Pound theory may be correct but incomplete, because free energies of small clusters are not calculated properly.

This assertion is supported by calculations of Feder et al (1966), which show that a 15% increase in surface tension restores agreement between Lothe-Pound theory and expansion cloud chamber experiments for water. Further evidence for the necessity of including small-cluster effects (including rotation and translation) is provided by recent molecular dynamics calculations of cluster free energies and by the successful use of these free energies for calculating the nucleation current by Burton (1973). Burton (1977) also observed that further work towards analytical solutions is required because his results are numerical rather than analytical. The analytical Fisher droplet model, combined with coexistence line data to determine free parameters [Kiang et al (1971)], has been successful in predicting experimental result; however, because it is derived by phenomenological principles, the model fails to describe the physics of the cluster well enough. As a possible new approach, Burton (1977) has suggested using Tolman's (1949) formula, Eq. (1-19), for surface tension instead of bulk surface tension in calculations of free energy, and that the parameter δ , which controls the surface tension variation with cluster size, be obtained from coexistence line data. In addition to a possible requirement that δ be a function of temperature, there is the conceptual difficulty that Tolman's formula is only valid at large cluster sizes. The surface free energy per surface molecule is the energy required to move a molecule from the interior to the surface [Hirschfelder, Curtis, and Bird (1954, p. 341)]; hence, the concept of surface tension loses its meaning for very small clusters where there are no interior molecules. Another problem with Burton's suggestion is that Tolman's (1949) formula is qualitatively correct; i.e., the sign of δ is positive [Briant and Burton (1975), Russanov and Brodskaya (1977),

and Dranova et al (1970)]. Therefore, as Wegener (1970) has observed, the increase in surface tension [reported by Feder et al (1966)] needed to bring the Lothe-Pound theory into agreement with water data is in the opposite direction from that predicted by the Tolman formula, Eq. (1-19), which implies that the surface tension at a small cluster is less than that for the bulk medium.

Our review of nucleation theory indicates lack of a complete derivation from basic principles. A theory based on first-principles would allow evaluation of the limits of the assumed master equation and investigation of the dynamics of condensation in detail - requirements for understanding why classical theory gives good agreement with diffusion cloud chamber experiments and for improving agreement with nozzle flow experiments. Our goal is to provide a complete first-principles derivation of nucleation theory. Lowry and Snider (1974) [and Snider and Lowry (1974)] have begun a quantum mechanics first-principles derivation by deriving a master equation for rates of dimer and trimer formation. They use bound states as a set of basis vectors and assume orthogonality among certain labeled channel states. As is well-known, the description of a physical system can be simplified by proper choice of a coordinate system. We can use many-body quantum mechanics to construct a natural coordinate system (in Hilbert space) for the nucleation problem if we assume that the eigenenergies (including translation) of a particular cluster configuration are unique. Also, the eigenenergies clearly define a cluster. Methods for developing master equations from many-body quantum mechanics are described by Fujita (1966). Extensions of these methods have been used successfully in deriving master equations

for laser physics [Haken (1974); Lax (1968), Louisell (1973); and Sargent, Scully and Lamb (1974)]. However, laser theory techniques are not adequate for the nucleation problem because they are not concerned with conservation of particles; i.e., photons have a zero chemical potential. Also, in nucleation theory one cannot assign the system and the reservoir to two separate entities as in laser theory. We use the techniques from laser physics, but make appropriate modifications for the nucleation problem.

In Ch. 2 we develop the quantum mechanics description of clusters from the vector formalism of Dirac (1958). We define a Hilbert space based on eigenenergies of molecular clusters, and construct a Fock space from the Hilbert basis vectors. The Hamiltonian operator is expanded in terms of Fock space creation and annihilation operators which model the nucleation process.

In Ch. 3 system and reservoir states are defined. Allowed forms of the interaction operator that must operate on both system and reservoir states are derived. The probability master equation follows from the reduced-density-matrix equation of motion.

In Ch. 4 the form of the interaction operator that controls the nucleation process is chosen. Two types of interactions are included: (1) scatterings that result in energy changes only and (2) interactions that result in changes in cluster size. The interaction operator is written as a product of system and reservoir operators. Steady-state solutions of the scattering part of the master equation yield energy level distribution functions. By computing average energies and numbers of clusters, we find that the Euler equation from thermodynamics is contained in the steady-state distribution function and that comparison

with thermodynamics determines the constants in the distribution function in terms of more familiar quantities such as temperature, pressure, and Boltzmann's constant.

Chapter 5 is devoted to solutions of the master equation. Both equilibrium and steady-state solutions are developed. Converting the monomer controlled master equation to a Fokker-Planck equation allows us to analyze the evolution toward a steady state and to determine a characteristic time for that process.

In Chapter 6 we outline general methods for obtaining equations of state from solutions of the master equation. For volumes less than saturation volume, we show that Bose-Einstein condensation occurs at temperatures near absolute zero, if there are no bound states, and that condensation by nucleation occurs otherwise. We derive an equation for a pressure-volume curve (along an isotherm) that has the familiar flat portion in the two-phase region and equations for specific volume, pressure, and number of clusters along the coexistence line. These equations are functions of the cluster Helmholtz free energies required for calculating steady-state nucleation currents; hence, the Tseng et al (1940) and Abraham (1968b) technique for obtaining effective surface tension (for nucleation calculations using the liquid-drop model) from coexistence line data is justified by our results.

In Chapter 7 we summarize rotational free energy formulae for clusters and propose a method for calculating their vibrational free energy. The vibrational free energy is analyzed by the Debye approximation of solid state physics. Anharmonic effects, necessary for the liquid phase, are included by perturbation analysis. Surface and interior molecules are allowed to have different Debye temperatures and

binding energies. A free-energy difference identified as the bulk surface tension occurs as a natural result.

Chapter 8 is concerned with the kinetic coefficients for changes in cluster size. We show how these coefficients are related to cross sections.

In Chapter 9 coexistence-line analysis and surface tension data yield necessary Debye temperatures and zero-point energies for water.

Finally, in Chapter 10, we use the data from Ch. 9 for calculating the nucleation current in diffusion cloud chamber experiments and the onset of condensation in nozzles. Our result agrees with the diffusion cloud chamber experiment as well as classical theory does. Comparison of our results with onset data from nozzle experiments is very encouraging. Comparison of our theory with classical and Lothe-Pound theory reveals that our equation for the steady-state current is very similar to that from the Lothe-Pound theory except for an extra term in the free energy, which is associated with variations of zero-point energy with cluster size.

We find that many of our results can be expressed as analytic convergent series known as Bose functions. Properties of these functions are given in App. I. The properties of the interaction operator in the interaction picture are derived in App II., and solutions of a Schrödinger-like master equation are given in App. III.

CHAPTER 2

APPLICATION OF MANY-BODY QUANTUM MECHANICS TO CLUSTERS OF MOLECULES

Our quantum mechanics description of clusters of molecules is based on the vector formalism proposed by Dirac (1958) and summarized by Fujita (1966) and Louisell (1973). The vector formalism allows direct derivation of the density operator, which provides the basis for a natural description of a system of single-particle cluster states in contact with a thermal reservoir. Given a time-dependent density operator for the composite system, the density operator for the single-particle states of each cluster can be found and, therefore, all the system's properties can be determined as the system evolves toward equilibrium. The density operator has been discussed in detail by Fano (1957). However, because of its fundamental contributions to quantum statistical mechanics, we will summarize some of its properties. This summary will review systems that are pure states, systems that are mixed states, and a composite system. The composite system can be regarded as an aggregate of two or more different groups of particles with operators that do not act on each other's eigenvectors. The total system operator is constructed from the operators for each of the groups of particles. We will show how the equation of motion for the density operator is obtained from Schrödinger's equation. Also, we will define eigenvectors for single-particle (or cluster) states and will construct the eigenvectors for a system of clusters in a Fock space. Appropriate creation and annihilation operators will be presented. These operators provide a necessary mechanism for allowing clusters of a given size to appear and

disappear from the system. Finally, we will review transformations from energy representation to the continuous momentum (or position) representation.

Consider a system in a pure quantum mechanical state represented by the ket vector $|\psi\rangle$. This vector consists of a linear combination of basis vectors $|a\rangle$, i.e.,

$$|\psi\rangle = \sum_a C_a |a\rangle . \quad (2-1)$$

The basis vectors are an orthogonal set,

$$\langle a | b \rangle = \delta_{ab} , \quad (2-2)$$

and satisfy the completeness relation,

$$\sum_a |a\rangle \langle a| = \hat{1} , \quad (2-3)$$

where $\hat{1}$ is the identity operator. Determination of $|\psi\rangle$ describes the system completely because it allows calculation of expected values of observables represented by Hermitian operators. The expected value of an operator $\hat{Q}$ is

$$\langle \hat{Q} \rangle_\psi = \langle \psi | \hat{Q} | \psi \rangle . \quad (2-4)$$

Some of our operators are not bounded operators, but can be replaced (for physically interesting portions of their spectra) by bounded operators. We shall assume this has been done where necessary. By inserting the resolution of the identity given by Eq. (2-3), into Eq. (2-4) and rearranging we obtain the following equation for the expectation value of the operator $\hat{Q}$,

$$\langle \hat{Q} \rangle_{\psi} = \sum_a \langle a | \hat{Q} | \psi \rangle \langle \psi | a \rangle . \quad (2-5)$$

The projection operator on $|\psi\rangle$ is

$$\hat{E}_{\psi} = |\psi\rangle \langle \psi| . \quad (2-6)$$

Equations (2-5) and (2-6) can be combined to give the expectation value in the form

$$\langle \hat{Q} \rangle_{\psi} = \text{tr} (\hat{Q} \hat{E}_{\psi}) = \text{tr} (\hat{E}_{\psi} \hat{Q}) , \quad (2-7)$$

where $\text{tr} ()$ is the trace, or sum, of the diagonal elements. The second equality of Eq. (2-7) is easily proven by use of the completeness relation. Equation (2-7) reveals that the projection operator $\hat{E}_{\psi}$ provides the necessary information about the system (which is in a pure state) as satisfactorily as the ket vector $|\psi\rangle$ does.

Next we consider a system that is an ensemble of many pure states. Such systems are necessary (1) because we cannot control initial conditions in many physically interesting cases, and (2) because they describe a composite system. The total wave function of an ensemble of states is normalized, but the different ket vectors $|\psi\rangle$ are not necessarily orthogonal. For an ensemble of $|\psi\rangle$'s, let $P(\psi)$ equal the probability of existence of a given $|\psi\rangle$. The superposition of mixed states allows us to write the expectation value of the operator $\hat{Q}$ in the composite system as

$$\langle \hat{Q} \rangle = \sum_{\psi} P(\psi) \langle \hat{Q} \rangle_{\psi} . \quad (2-8)$$

If we define a density operator as

$$\hat{\rho} = \sum_{\psi} |\psi\rangle P(\psi) \langle\psi|, \quad (2-9)$$

Eqs. (2-5), (2-8) and (2-9) can be combined and the identity operator used to show that

$$\langle\hat{Q}\rangle = \text{tr} (\hat{Q} \hat{\rho}) = \text{tr} (\hat{\rho} \hat{Q}). \quad (2-10)$$

The definition, Eq. (2-9), provides the density operator for both pure and mixed states. The density operator has the property

$$\text{tr} (\hat{\rho}) = 1, \quad (2-11)$$

which follows from the use of the completeness relation and from the requirement that the sum of the probabilities, $P(\psi)$, be unity. The density operator also has the property

$$\langle\hat{\rho}\rangle = \text{tr} (\hat{\rho}^2) \leq 1, \quad (2-12)$$

which follows from the definition, the completeness relation, and the Schwarz inequality, i.e., from

$$\begin{aligned} \text{tr} (\hat{\rho}^2) &= \sum_{\phi, \psi} |\langle\psi|\phi\rangle|^2 P(\psi) P(\phi) \\ &\leq \sum_{\phi, \psi} \langle\psi|\psi\rangle \langle\phi|\phi\rangle P(\psi) P(\phi) = 1. \end{aligned} \quad (2-13)$$

The equality holds if, and only if, ψ and ϕ represent the same state. For a pure state, $\langle \hat{\rho} \rangle = 1$, and for a mixed state, $\langle \hat{\rho} \rangle < 1$.

Next, consider the method of calculating expectation values in a composite system, AB. Ket vectors in this system are formed from direct products of basis vectors,

$$| \psi_{AB} \rangle = | a \rangle \otimes | b \rangle \equiv | a, b \rangle. \quad (2-14)$$

If $\hat{Q}_A$ is an operator in System A, we must write $\hat{Q}$ in a form that covers the whole system, i.e.,

$$\hat{Q} = \hat{Q}_A \otimes \hat{1}_B, \quad (2-15)$$

where $\hat{1}_B$ is the identity operator in System B. For a composite system of mixed states, the density operator, $\hat{\rho}_{AB}$, is a special operator because, in general,

$$\hat{\rho}_{AB} \neq \hat{\rho}_A \otimes \hat{\rho}_B. \quad (2-16)$$

To prove this statement, note that the composite of mixed states,

$$| \psi_{AB} \rangle = C_1 | a_1, b_1 \rangle + C_2 | a_2, b_2 \rangle, \quad (2-17)$$

has the projection operator

$$\begin{aligned} | \psi_{AB} \rangle \langle \psi_{AB} | &= | C_1 |^2 | a_1, b_1 \rangle \langle a_1, b_1 | \\ &+ | C_2 |^2 | a_2, b_2 \rangle \langle a_2, b_2 | \\ &+ C_1 C_2^* | a_1, b_1 \rangle \langle a_2, b_2 | + C_1^* C_2 | a_2, b_2 \rangle \langle a_1, b_1 |. \end{aligned} \quad (2-18)$$

The cross terms expand the covering space beyond the region covered by a simple direct product of vectors. This implies that the density

operator cannot be constructed from eigenvectors in the general case. Although the density operator for a composite system cannot be constructed from its components, we can perform the opposite operation, i.e., given $\hat{\rho}_{AB}$, we can determine $\hat{\rho}_A$ or $\hat{\rho}_B$. To demonstrate that this is possible, calculate the expectation value of the operator $\hat{Q}$, given by Eq. (2-15):

$$\langle \hat{Q} \rangle = \sum_{\psi_{AB}} \langle \psi_{AB} | \hat{Q} | \psi_{AB} \rangle P(\psi_{AB}) . \quad (2-19)$$

If a density operator is defined as

$$\hat{\rho}_{AB} \equiv \sum_{\psi_{AB}} | \psi_{AB} \rangle P(\psi_{AB}) \langle \psi_{AB} | , \quad (2-20)$$

the completeness relation can be used, and terms in Eq. (2-19) can be rearranged to show that

$$\langle \hat{Q} \rangle = \sum_{a,b} \langle a, b | \hat{Q} \hat{\rho}_{AB} | a, b \rangle . \quad (2-21)$$

Inserting Eq. (2-15) into Eq. (2-21) and rearranging operators and vectors that commute gives,

$$\langle \hat{Q} \rangle = \sum_{a,b} \langle a | \hat{Q}_A \langle b | \hat{\rho}_{AB} | b, a \rangle . \quad (2-22)$$

Let a density operator for System A be defined as

$$\hat{\rho}_A \equiv \sum_b \langle b | \hat{\rho}_{AB} | b \rangle = \text{tr}_B (\hat{\rho}_{AB}) , \quad (2-23)$$

then Eq. (2-22) can be rewritten as

$$\langle \hat{Q} \rangle = \text{tr}_A (\hat{\rho}_A \hat{Q}) = \text{tr}_A (\hat{Q} \hat{\rho}_A) \quad (2-24)$$

Equation (2-23) shows that the density operator for any component of a composite system can be found by tracing over all the other components. This feature makes the density operator particularly useful for analyzing the evolution of a set of molecular clusters. The composite system is a set of cluster states and thermal reservoir states. Given the density operator for such a composition, the density operator for cluster states can be found by tracing over quantum numbers corresponding to the reservoir.

Because we are only interested in calculating average values of observables, Eqs. (2-23) and (2-24) are the basis for further development. These equations are only useful if a means of obtaining the density operator is available. The density operator can be obtained from the solution of an equation of motion for the density operator. Such an equation of motion can be found by differentiating Eq. (2-20) with respect to time and using the Schrödinger equation,

$$i \hbar \frac{\partial}{\partial t} | \psi_{AB} \rangle = \hat{H}_T | \psi_{AB} \rangle , \quad (2-25)$$

where $\hat{H}_T$ is the usual Hamiltonian operator. The result is

$$i \hbar \frac{\partial \hat{\rho}_{AB}}{\partial t} = - \left[\hat{\rho}_{AB}, \hat{H}_T \right] . \quad (2-26)$$

The subscript AB is intended to imply a density operator for any composite system: i.e., we are not limited to two components only. In deriving Eq. (2-26) we used the relation $\partial P(\psi_{AB})/\partial t = 0$, because the equations are in the Schrödinger picture where all time dependence is contained in the eigenvectors [see Dirac (1958, p. 123)].

Equation (2-26) is the quantum mechanical analog of the classical Liouville equation of motion for a system of particles in phase space,

$$\frac{\partial f(p,q)}{\partial t} = - \left\{ f(p,q), H \right\} , \quad (2-27)$$

where $\{, \}$ is the Poisson bracket and $f(p,q)$ is the distribution function in phase space (p = momentum, q = position). Classical approaches to nonequilibrium problems concentrate on solving Eq. (2-27) [see, for example, Prigogine (1962)]. Because classical mechanics is a limiting case of quantum mechanics, we prefer to concentrate on solving Eq. (2-26).

Solution of Eq. (2-26) provides the density operator needed to calculate component density operators and average values of operators by taking the trace defined by Eqs. (2-23) and (2-24). Execution of the solution and trace requires a definition of the Hilbert space for each component and for the composite. The Hilbert space is defined (1) by identification of the basis vectors of each component and (2) by the effect of Operator $\hat{H}_T$ on the basis vectors of each component and on the vectors that define the Hilbert space of the composite. We can choose a set of basis vectors of each part of the composite by defining $\hat{H}_T$ to consist of a sum of terms, each of which is diagonal in the representation of a particular component or is an interaction term which is

not diagonal. A basis vector for the composite is found by taking the direct product of basis vectors of all the components as required by Eq. (2-14). This implies that the interaction part of $\hat{H}_T$ is a product of operators, each of which is defined in the Hilbert space of a particular component.

Our next step is to define sets of basis vectors that can be used to define clusters (or molecules in a mixture); however, it is convenient to define our methods of labeling sets of quantum numbers before proceeding to this task.

We will use greek letters to identify cluster size. Let $n_{i\alpha}$ be the number of times a cluster of α molecules appears in the i^{th} energy state of that cluster. The i^{th} energy state is then represented by a certain value assigned to each of a set of quantum numbers. The energy of this state can include the energy of translation, rotation, and vibration. Eventually, it will be necessary to distinguish the various kinds of energy; therefore, we adopt the following notation convention for subscripts.

i or $i(T)$ for all energy states,

$i(K)$ for center-of-mass translation energy states,

$i(R)$ for rotation energy states,

$i(V)$ for internal vibrational energy states, and

$i(I)$ for internal energy states.

This convention also implies the following identities:

$$i(I) \equiv (i(V), i(R))$$

$$i \equiv i(T) \equiv (i(I), i(K)) \equiv (i(V), i(R), i(K)) \quad .$$

It is understood that each set of quantum numbers, i , is associated with a particular cluster size α . In cases where the association is not obvious, we write $i(\alpha)$ or $[i(T)](\alpha)$.

For the special case of $n_{i\alpha} = 1$, a single-particle state exists. Probabilities of specific cluster sizes are determined in the Hilbert space of single-particle states. We denote the single-particle state as

$$| \psi_{i\alpha} \rangle = | i\alpha \rangle = | n_{i\alpha} = 1 \rangle . \quad (2-28)$$

The single-particle states are found from solutions of the time-independent Schrödinger equation,

$$\hat{H}_0 | i\alpha \rangle = \epsilon_{i\alpha} | i\alpha \rangle . \quad (2-29)$$

Because they are eigenvectors, these states are considered to be orthogonal,

$$\langle i\alpha | j\beta \rangle = \delta_{ij} \delta_{\alpha\beta} , \quad (2-30)$$

and to obey the completeness relation

$$\sum_{i\alpha} | i\alpha \rangle \langle i\alpha | = \hat{1} . \quad (2-31)$$

In the Hilbert space of single particle states, which we denote by $H^{(1)}$, the operator $a_{i\alpha}$ annihilates a cluster in a given energy state, i.e.,

$$a_{i\alpha} | j\beta \rangle = \delta_{ij} \delta_{\alpha\beta} | \text{vac} \rangle , \quad (2-32)$$

in terms of the vacuum state $| \text{vac} \rangle$. Taking the adjoint of Eq. (2-32) gives

$$\langle j\beta | a_{i\alpha}^\dagger = \delta_{ij} \delta_{\alpha\beta} \langle \text{vac} | .$$

To discover the role of the adjoint operator, $a_{i\alpha}^\dagger$, consider $a_{i\alpha}^\dagger | j\beta \rangle$. By operating on this ket vector with the identity operator from Eq. (2-31); using the orthogonality condition, Eq. (2-30); and using the above equation; we obtain

$$a_{i\alpha}^\dagger | j\beta \rangle = \delta_{j\beta, \text{vac}} | i\alpha \rangle . \quad (2-33)$$

The operator $a_{i\alpha}^\dagger$ plays the role of creating a cluster, in the energy level specified by the subscript, from the vacuum state. Creation and annihilation operators will also be defined in Fock space; hence, they provide the mechanism for transformation from one space to the other.

In the Hilbert space $H^{(1)}$, the commutator of creation and annihilation operators does not have any meaning; however, the following relation, which is obtained from Eqs. (2-32) and (2-33), can be used in lieu of a commutator:

$$a_{i\alpha} a_{j\beta}^\dagger = \delta_{ij} \delta_{\alpha\beta} \hat{1} . \quad (2-34)$$

It is observed by Louisell (1973, p. 202) that these creation and annihilation operators can be represented by another set of operators in the same Hilbert space by the following correspondence:

$$a_{i\alpha} \rightarrow | \text{vac} \rangle \langle i \alpha | , \quad a_{i\alpha}^\dagger \rightarrow | i \alpha \rangle \langle \text{vac} | ,$$

$$\langle \text{vac} | \text{vac} \rangle = 1 , \quad | \text{vac} \rangle \langle \text{vac} | = \hat{1} .$$

The single-particle states can be used to construct a quantum mechanics description of the complete system. The basis vectors for such a system can be formed by attaching a particle label to each of the ket vectors from Eq. (2-28), forming a direct product of all of them, and summing over all permutations of particle labels to obtain

$$\begin{aligned} | \psi \rangle_a &= \frac{1}{\sqrt{N!}} \sum_P \hat{P} | (i\alpha)_1, (j\beta)_2, \dots, (k\gamma)_N \rangle \\ &= | i\alpha \dots k\gamma \rangle_{a, N} \end{aligned} \quad (2-35)$$

and

$$\begin{aligned} | \psi \rangle_s &= \frac{1}{\sqrt{N!}} \sum_P \hat{P} | (i\alpha)_1, (j\beta)_2, \dots, (k\gamma)_N \rangle \\ &= | i\alpha \dots j\beta \rangle_{s, N} \end{aligned} \quad (2-36)$$

In the above equations, we have used the notation of Dirac (1958), where N is the total number of particles, $\hat{P}$ is the permutation operator, and $\sum_P$ is the sum over all permutations. For the antisymmetric case, Eq. (2-35), the plus and minus signs correspond, respectively, to even or odd numbers of permutations of particle labels in the basic ket to obtain to a given state. The symmetric case is given by Eq. (2-36). The symmetric case corresponds to boson particles and the antisymmetric case corresponds to fermion particles. Because the number of fermions

in each energy state is 0 or 1, see Fujita (1966, p. 16), the population is restricted and condensation is unlikely to occur. Hence, we shall consider clusters to be bosons and concentrate on symmetric states, Eq. (2-36). The subscript s will be dropped and all states will be assumed to be symmetric. The Hilbert space of Eq. (2-36) will be identified by H .

For mixed states, each state represented by a ket in the direct product of states in Eq. (2-36) can be occupied by several particles. By counting states of indistinguishable particles, see Dirac (1958, p. 226), it can be shown that the norm of Eq. (2-36) is

$$\langle i\alpha \dots k\gamma | i\alpha \dots k\gamma \rangle_N = n_{i\alpha}! n_{j\beta}! \dots n_{k\gamma}! \quad (2-37)$$

The number of clusters is found from

$$N = \sum_{i\alpha} n_{i\alpha} \quad (2-38)$$

The ket of Eq. (2-36) can be generalized to allow for a variable N by composing a ket that consists of a sum of kets formed from all possible values of N [Dirac (1958, p. 227)],

$$\begin{aligned} |\psi\rangle &= |\text{vac}\rangle + |i\alpha\rangle_1 + |i\alpha, j\beta\rangle_2 + \dots \\ &= \sum_N |i\alpha \dots k\gamma\rangle_N \end{aligned} \quad (2-39)$$

The space of Eq. (2-39) is a collection of many Hilbert spaces $H^{(N)}$ and is called Fock space; see Jauch (1968, p. 281). The Fock space,

$$F = H^{(0)} \otimes H^{(1)} \otimes H^{(2)} \otimes \dots ,$$

is adaptable to describing a system of clusters because the number of particles is variable.

The kets of Eq. (2-39) are inconvenient to work with; we need, therefore, another, equivalent, representation. Instead of recording the state of every particle as suggested by Eq. (2-39), we can list the available energy states and the number of particles in each state. Then, the basic kets can be written as:

$$| n_{11} \dots n_{i\alpha} \dots n_{\infty} \rangle .$$

These kets, which are also in the Fock space, obey the Schrödinger equation

$$\hat{H}_0 | n_{11} \dots n_{i\alpha} \dots n_{\infty} \rangle = (n_{11} \epsilon_{11} + \dots + n_{i\alpha} \epsilon_{i\alpha} + \dots + n_{\infty} \epsilon_{\infty})$$

$$| n_{11} \dots n_{i\alpha} \dots n_{\infty} \rangle , \quad (2-40)$$

are orthogonal,

$$\begin{aligned} & \langle n'_{11} \dots n'_{i\alpha} \dots n'_{\infty} | n_{11} \dots n_{i\alpha} \dots n_{\infty} \rangle \\ &= \delta'_{n_{11} n_{11}} \dots \delta'_{n_{i\alpha} n_{i\alpha}} \dots \delta'_{n_{\infty} n_{\infty}} , \end{aligned} \quad (2-41)$$

have a completeness relation,

$$\sum_{\{n\}} | n_{11} \dots n_{i\alpha} \dots n_{\infty} \rangle \langle n_{11} \dots n_{i\alpha} \dots n_{\infty} | = \hat{1} , \quad (2-42)$$

and, therefore, form a complete set of basis vectors. We use the notation

$$\sum_{\{n\}} \equiv \sum_{n_{11}=0}^{\infty} \sum_{n_{21}=0}^{\infty} \cdots \sum_{n_{\infty 1}=0}^{\infty} \cdots \sum_{n_{i\alpha}=0}^{\infty} \cdots \sum_{n_{\infty\infty}=0}^{\infty} . \quad (2-43)$$

The annihilation operator of Eq. (2-32) can also be defined in the number representation; however, we label it $b_{i\alpha}$ to emphasize that it is defined in a different representation of the vector space. By definition,

$$\begin{aligned} & b_{i\alpha} | n_{11} \dots n_{i\alpha} \dots n_{\infty\infty} \rangle \\ &= C(n_{i\alpha}) | n_{11} \dots (n_{i\alpha}-1) \dots n_{\infty\infty} \rangle , \end{aligned} \quad (2-44)$$

where $C(n_{i\alpha})$ is a normalization constant. By operating on the adjoint of Eq. (2-44) with the identity operator and by using the orthogonality condition, Eq. (2-41), we find the function of the adjoint of $b_{i\alpha}$:

$$\begin{aligned} & b_{i\alpha}^{\dagger} | n_{11} \dots n_{i\alpha} \dots n_{\infty\infty} \rangle \\ &= C^*(n_{i\alpha}+1) | n_{11} \dots (n_{i\alpha}+1) \dots n_{\infty\infty} \rangle . \end{aligned} \quad (2-45)$$

Equations (2-44) and (2-45) reveal the reasons for referring to $b_{i\alpha}$ as the annihilation operator and to $b_{i\alpha}^{\dagger}$ as the creation operator. To find the normalization constant $C(n_{i\alpha})$, we compute

$$\begin{aligned}
& b_{i\alpha}^\dagger b_{i\alpha} | n_{11} \dots n_{i\alpha} \dots n_{\infty} \rangle \\
& = | C(n_{i\alpha}) |^2 | n_{11} \dots n_{i\alpha} \dots n_{\infty} \rangle .
\end{aligned} \tag{2-46}$$

This is an eigenvalue equation which indicates that the operator is a Hermitian operator for the number representation and that its eigenvalue is $|C(n_{i\alpha})|^2$. Hence, from physical interpretation (and also by analogy with the harmonic oscillator problem), we find that the number in a given state is

$$| C(n_{i\alpha}) |^2 = n_{i\alpha} , \tag{2-47}$$

and define

$$b_{i\alpha}^\dagger b_{i\alpha} = \hat{n}_{i\alpha} , \tag{2-48}$$

as a number operator. Equations (2-44) through (2-48) combine to give the familiar operator equations:

$$\begin{aligned}
& b_i | n_{11} \dots n_{i\alpha} \dots n_{\infty} \rangle \\
& = \sqrt{n_{i\alpha}} | n_{11} \dots (n_{i\alpha}-1) \dots n_{\infty} \rangle ,
\end{aligned} \tag{2-49}$$

$$\begin{aligned}
& b_{i\alpha}^\dagger | n_{11} \dots n_{i\alpha} \dots n_{\infty} \rangle \\
& = \sqrt{n_{i\alpha}+1} | n_{11} \dots (n_{i\alpha}+1) \dots n_{\infty} \rangle ,
\end{aligned} \tag{2-50}$$

$$\begin{aligned} & \hat{n}_{i\alpha} | n_{11} \dots n_{i\alpha} \dots n_{\infty} \rangle \\ & = n_{i\alpha} | n_{11} \dots n_{i\alpha} \dots n_{\infty} \rangle . \end{aligned} \quad (2-51)$$

From Eqs. (2-49) and (2-50), the commutation relations for the creation and annihilation operators can be found:

$$[b_{i\alpha}, b_{i\alpha}^{\dagger}] = \delta_{ij} \delta_{\alpha\beta} \hat{1} , \quad (2-52)$$

$$[b_{i\alpha}, b_{i\alpha}] = [b_{i\alpha}^{\dagger}, b_{i\alpha}^{\dagger}] = 0 . \quad (2-53)$$

Repeated use of Eq. (2-50) yields the important relation,

$$\begin{aligned} & | n_{11} \dots n_{i\alpha} \dots n_{\infty} \rangle \\ & = \frac{(b_{11}^{\dagger})^{n_{11}} \dots (b_{i\alpha}^{\dagger})^{n_{i\alpha}} \dots (b_{\infty}^{\dagger})^{n_{\infty}}}{\sqrt{n_{11}! \dots n_{i\alpha}! \dots n_{\infty}!}} | \text{vac} \rangle , \end{aligned} \quad (2-54)$$

where $| \text{vac} \rangle$ is the direct product of vacuum states for all cluster sizes.

Consider the ket vectors formed by substituting different sets of numbers, $\{ n_{i\alpha} \}$, in the ket

$$(b_{11}^{\dagger})^{n_{11}} \dots (b_{i\alpha}^{\dagger})^{n_{i\alpha}} \dots (b_{\infty}^{\dagger})^{n_{\infty}} \dots | \text{vac} \rangle .$$

Dirac (1958) observes that these kets form a complete set of vectors, all of which are orthogonal to each other, each with a squared length of

$$n_{11}! \dots n_{i\alpha}! \dots n_{\infty\infty}! \dots$$

This result can be derived from Eqs. (2-54) and (2-41). Recalling Eq. (2-37), it can be seen that these kets have the same properties as the kets of Eq. (2-39); thus, kets referring to the same set $\{ n_{i\alpha} \}$ can be equated without any inconsistency. Hence, we identify

$$| \psi \rangle = | \{ n \} \rangle \equiv | n_{11} \dots n_{i\alpha} \dots n_{\infty\infty} \rangle , \quad (2-55)$$

as the ket for a system of clusters considered to be bosons. The number representation for bosons is mathematically the same as an assembly of interacting harmonic oscillators; however, the eigenenergies are of a more general nature and also more difficult to obtain. Equation (2-55) allows us to consider $b_{i\alpha}^\dagger$ and $b_{i\alpha}$ as operators defined in Fock space.

Employment of the number representation, requires that the Hamiltonian operator $\hat{H}_T$ be expanded in terms of creation and annihilation operators. The Hamiltonian can be written

$$\hat{H}_T = \hat{H}_O + \hat{V} , \quad (2-56)$$

where $\hat{H}_O$ is the part of the operator that is diagonal in $H^{(1)}$ or F , as implied by Eqs. (2-29) and (2-40), respectively; the $\hat{V}$ is an interaction term and its expansion will depend on the particular physical processes

which it represents. Because the number operator is diagonal in both $H^{(1)}$ and F it is convenient to expand in terms of this operator, i.e.,

$$\hat{H}_0 = \hbar \sum_{i\alpha} \omega_{i\alpha} c_{i\alpha}^\dagger c_{i\alpha} \quad , \quad (2-57)$$

and hence preserve the diagonal properties of $\hat{H}_0$. The operators $c_{i\alpha}^\dagger$ and $c_{i\alpha}$ are creation and annihilation operators, respectively, defined in both $H^{(1)}$ and F , i.e., they could be either $a_{i\alpha}^\dagger$ and $a_{i\alpha}$ or $b_{i\alpha}^\dagger$ and $b_{i\alpha}$. To calculate the expansion coefficient we let $\hat{H}_0$ operate on the single-particle state, $|j\beta\rangle$, and use Eqs. (2-32) and (2-33) in connection with the properties of the delta function (to complete the sum) and Eq. (2-29). The result is

$$\hbar \omega_{i\alpha} = \epsilon_{i\alpha} \quad . \quad (2-58)$$

Substitution of Eq. (2-58) into Eq. (2-57), followed by operation on $|\{n\}\rangle$ (in F) with the resultant $\hat{H}_0$ and use of Eqs. (2-48) and (2-51) yields the Schrödinger equation, Eq. (2-40). Hence, the eigenvalue operator is defined in both $H^{(1)}$ and F as

$$\hat{H}_0 = \sum_{i\alpha} \epsilon_{i\alpha} c_{i\alpha}^\dagger c_{i\alpha} \quad . \quad (2-59)$$

The Schrödinger equations, Eqs. (2-29) and (2-40), are diagonal in the energy representation; however, the Hamiltonian operator is generally a function of position and momentum. This implies that transformations from energy representations to representations in which momentum operators

$\hat{p}$ or position operators $\hat{q}$ are diagonal will be required to calculate eigenenergies $\epsilon_{i\alpha}$. The standard Dirac procedure is to introduce a continuous space where the position operators $\hat{q}$ obey the eigenvalue equation,

$$\hat{q} | q \rangle = q | q \rangle , \quad (2-60)$$

are orthogonal,

$$\langle q | q' \rangle = \delta(q - q') , \quad (2-61)$$

and form an identity operator

$$\int dq | q \rangle \langle q | = \hat{1} . \quad (2-62)$$

By taking a scalar product of the bra vector $\langle q |$ with each side of Eq. (2-29),

$$\langle q | \hat{H}_0(\hat{p}, \hat{q}) | i\alpha \rangle = \epsilon_{i\alpha} \langle q | i\alpha \rangle , \quad (2-63)$$

Louisell (1973, p. 41) derives a general theorem,

$$\langle q | F(\hat{p}) | i \rangle = F\left(\frac{\hbar}{i} \frac{\partial}{\partial q}\right) \langle q | i \rangle . \quad (2-64)$$

By series expansion and use of Eq. (2-60) it can generally be shown that

$$F(\hat{q}) | q \rangle = F(q) | q \rangle . \quad (2-65)$$

The quantity, $\langle q | i \rangle$, i.e., the expansion coefficient for transformation from a position to an energy representation, is the usual wave function and is identified as

$$\psi_i(q) \equiv \langle q | i \rangle . \quad (2-66)$$

The position and the momentum dependence of the Hamiltonian operator can usually be separated, i.e.,

$$H_0(\hat{q}, \hat{p}) = H_0(\hat{p}) + H_0(\hat{q}) ; \quad (2-67)$$

hence, we can use Eqs. (2-63) through (2-66) to find the usual Schrödinger wave equation, a partial differential equation that must be solved to obtain the eigenenergies $\epsilon_{i\alpha}$:

$$H_0\left(\frac{\hbar}{i} \frac{\partial}{\partial q}, q\right) \psi_{i\alpha}(q) = \epsilon_{i\alpha} \psi_{i\alpha}(q) . \quad (2-68)$$

CHAPTER 3

MASTER EQUATION FOR SYSTEMS IN CONTACT WITH A THERMAL RESERVOIR

In Chapter 2 we outlined a method of using the composite density operator $\hat{\rho}_{AB}$ to find the component density operators $\hat{\rho}_A$ and $\hat{\rho}_B$, providing Eq. (2-26) could be solved. In this chapter we shall be more specific about the definitions of the components of the density operator and reduce the equation of motion, Eq. (2-26), to a probability master equation for one of the components. We previously defined an orthogonal set of basis vectors in both $H^{(1)}$ or F . The component density operators can be defined in either space. For the nucleation problem we wish to identify clusters as groups of molecules bound together. A cluster can be identified by a set of eigenenergies that represent the bound state of a given number of molecules. The eigenvectors of each cluster size form a set of basis vectors for single-particle states. The single-particle states are also pure states. We wish to calculate the probability of finding a certain particle defined by a single-particle state when the entire composite system is sampled. This is most easily accomplished if one of the components of the density operator is defined in $H^{(1)}$. Upon sampling the composite system in search of a particular state, measurements give a value of unity (if the state is found) or of zero (if the state is not found). The probability of a given state is the number of measurements that result in unity divided by the total number of measurements. This probability can be computed in $H^{(1)}$ by taking a scalar product. Note that in $H^{(1)}$ the number operator has an expectation value of zero or one, i.e., from Eqs. (2-32) and (2-33):

$$\langle j\beta | a_{i\alpha}^\dagger a_{i\alpha} | j\beta \rangle = \delta_{ij} \delta_{\alpha\beta} \quad ,$$

where $|j\beta\rangle$ is the sampled state and $a_{i\alpha}^\dagger a_{i\alpha}$ is the number operator of the state we are searching for. To be consistent with the usual nomenclature we call the single-particle states the "system". The single-particle states (which are the pure states or system states in $H^{(1)}$), combine in many ways to form a set of basis vectors that are diagonal in the number representation of Fock space. The Fock space is a quantum description of the entire set of clusters (plus any other gases that may be present). The Fock space basis vectors are built up from single-particle states and do not contain an energy of interaction. In a real system one expects the single-particle states (or wave functions) to overlap and, hence, to interact with a mixture of states we describe by a number representation in Fock space. Let us investigate the time-dependent evolution of such an interaction. As noted in Chapter 2 this can be accomplished by forming a composite vector from the direct product of two vectors; therefore, we form the composite by taking the direct product of the single-particle states in $H^{(1)}$ with the basis-vector states in F . An interaction operator can be defined to operate on this composite vector space by constructing the operator as a product of operators defined in either of the two spaces. The Fock space represents an infinite number of states each single-particle state can interact with, and therefore can be considered as a reservoir of states. To follow the usual nomenclature we call the set of states in Fock space the "reservoir". We shall denote the components A and B of $\hat{\rho}_{AB}$ as R and S, for reservoir and system, respectively.

Our derivation of the master equation relies, to a large extent, on techniques and interpretations given by Louisell (1973, Ch. 6). The

major differences are: (1) we have made use of the fact that the diagonal part of the Hamiltonian [as defined by Eq. (2-57)] can include terms common to both the system and the reservoir, and (2) the use of the properties of creation and annihilation operators in $H^{(1)}$ and F (see App. II) to write the time-dependent interaction operator in a factorable form [Eq. (II-2)]. These changes are important in application to nucleation theory because the restriction of considering the reservoir as a separate equilibrium system is eliminated. We also apply some of Louisell's techniques (1973, p. 198) to define restrictions on parts of the interaction operator in $H^{(1)}$ more explicitly than has been done in the past. Although this derivation is less general than Louisell's, because our reservoir operators must be defined in terms of creation and annihilation operators, we no longer have to assume that the diagonal part of the Hamiltonian, which operates on the reservoir states, commutes with the reservoir density operator $\hat{\rho}_R$.

The equation of motion, Eq. (2-26), is in the Schrödinger picture. Because the part of the Hamiltonian which is diagonal in the energy representation is constant in time, we can perform a transformation to an interaction picture and thereby obtain an equation of motion in terms of the weak interaction between a system and a reservoir. This equation can be solved by an approximate second-order expansion before transforming back to the Schrödinger picture. After identification of parts of the interaction operator as system and reservoir operator terms in a second-order expansion, traces can be taken over reservoir states to obtain an equation of motion for the system density operator. This equation of motion is different from those obtained from pure second order-expansion of the Schrödinger equation because the reservoir

acts as a damping mechanism. Finally, a probability master equation will be derived by taking scalar products of the density operator equation of motion with single-particle state vectors.

To associate density operators with a certain picture, we shall use superscripts: (1) s, for the Schrödinger picture, (2) h, for the Heisenberg picture; and (3) i, for the interaction picture. We shall use the subscripts: (1) RS, to identify the composite system, (2) R, to identify the reservoir, and (3) S, to identify the system. In this notation, the equation of motion for the density operator, Eq. (2-26), can be written as:

$$\frac{\partial \hat{\rho}_{RS}^s(t)}{\partial t} = - \frac{1}{i\hbar} [\hat{\rho}_{RS}^s(t), \hat{H}_T] \quad (3-1)$$

The density operator $\hat{\rho}_{RS}^s(t)$ contains more information than is required; however, $\hat{\rho}_S$ can be obtained by taking the trace over the reservoir as Eq. (2-23) implies. In the Schrödinger picture all the motion is in the eigenvectors (or density operator), and the Hamiltonian operator is constant in time. The density operator is the only operator that is a function of time in the Schrödinger picture.

Equation (3-1) can only be solved by approximate methods. To accomplish this, we transform this equation to an interaction picture (where the high-energy components of the Hamiltonian operator are implicit) before making approximations. The transformation can be implemented by using the Hamiltonian in the form given by Eq. (2-56), which can also be written as

$$\hat{H}_T = \hat{H}_0 + \sum_J \hat{V}_J \quad , \quad (3-2)$$

where each V_J represents a different interaction process.

We may write the Schrödinger equation in F (or $H^{(1)}$) as

$$i\hbar \frac{\partial}{\partial t} | \phi^S(t) \rangle = \hat{H}_0 | \phi^S(t) \rangle . \quad (3-3)$$

The operator $\hat{U}(t, t_0)$ is defined as one which transforms the stationary eigenvectors of the Heisenberg representation, $| \phi^h \rangle$, to the Schrödinger representation, i.e.,

$$\hat{U}(t, t_0) | \phi^h \rangle = | \phi^S(t) \rangle . \quad (3-4)$$

From Eq. (3-3) and (3-4), it follows that

$$\hat{U}(t, t_0) = e^{-\frac{i}{\hbar} (t-t_0) \hat{H}_0} . \quad (3-5)$$

Equation (3-5) indicates that $\hat{U}(t, t_0)$ is a unitary operator. It may also be used to define a density operator in the interaction picture by a similarity transform which preserves the Hermitian character of the density operator:

$$\hat{\rho}_{RS}^S(t) = \hat{U}(t, t_0) \hat{\rho}_{RS}^i(t) \hat{U}(t, t_0)^{-1} . \quad (3-6)$$

Equations (3-1), (3-2), (3-5), and (3-6) can be combined to find a partial differential equation for $\hat{\rho}_{RS}^i(t)$. If we define an interaction operator in the interaction picture as

$$\hat{V}_J(t-t_0) \equiv \hat{U}(t, t_0)^{-1} \hat{V}_J \hat{U}(t, t_0) , \quad (3-7)$$

the result is

$$\frac{\partial \hat{\rho}_{RS}^i(t)}{\partial t} = - \frac{1}{i\hbar} \sum_J [\hat{\rho}_{RS}^i(t), \hat{V}_J(t-t_0)] \quad (3-8)$$

An intermediate step, the result of differentiating Eq. (3-6), is

$$\frac{\partial \hat{\rho}_{RS}^s(t)}{\partial t} = \hat{U}(t, t_0) \left\{ \frac{\partial \hat{\rho}_{RS}^i(t)}{\partial t} - \frac{1}{i\hbar} [\hat{\rho}_{RS}^i(t), \hat{H}_0] \right\} \hat{U}(t, t_0)^{-1} \quad (3-9)$$

The two equations, Eqs. (3-8) and (3-9), are equivalent to the equation of motion represented by Eq. (3-1). The advantage of this form is that Eq. (3-8) is a differential equation for $\hat{\rho}_{RS}^i(t)$ which is a function of a weak interaction operator. Approximate solutions of Eq. (3-8) can be substituted into Eq. (3-9) to obtain the desired equation of motion.

Another form of Eq. (3-8) may be obtained by integration and successive substitution. The result after two substitutions is

$$\begin{aligned} \hat{\rho}_{RS}^i(t) = & \hat{\rho}_{RS}^i(t_0) + \frac{1}{i\hbar} \sum_I \int_{t_0}^t dt' [\hat{V}_I(t'-t_0), \hat{\rho}_{RS}^i(t_0)] \\ & + \frac{1}{(i\hbar)^2} \sum_{JK} \int_{t_0}^t dt' \int_{t_0}^t dt'' [\hat{V}_J(t'-t_0), [\hat{V}_K(t''-t_0), \hat{\rho}_{RS}^i(t'')]] \quad (3-10) \end{aligned}$$

If the time interval, $t-t_0$, is short enough, i.e.,

$$(t-t_0) \ll \gamma^{-1} \quad , \quad (3-11)$$

where γ^{-1} is a damping time for $\hat{\rho}_{RS}^i(t)$, we can take

$$\hat{\rho}_{RS}^i(t'') \approx \hat{\rho}_{RS}^i(t_0) \quad (3-12)$$

in the integral of Eq. (3-10).

If the interaction operator, $\hat{V}_J$, can be written as the product of two operators: (1) $\hat{Q}_J$ defined in $H^{(1)}$ and (2) $\hat{F}_J$ defined in F . i.e.,

$$\hat{V}_J = \hat{H} \hat{Q}_J \hat{F}_J \quad ; \quad (3-13)$$

it is proven in Appendix II that

$$\hat{V}_J(t-t_0) = \hat{V}_J e^{i\Omega_J(t-t_0)} \quad , \quad (3-14)$$

where Ω_J (a number) is determined from the form of $\hat{Q}_J$ and $\hat{F}_J$. Substitution of Eq. (3-12) for $\hat{\rho}_{RS}^i(t'')$ and Eq. (3-14) for $\hat{V}_J(t-t_0)$ into Eq. (3-10) leaves the equation for the density operator in the interaction picture as

$$\begin{aligned} \hat{\rho}_{RS}^i(t) = & \hat{\rho}_{RS}^i(t_0) + \frac{1}{i\hbar} \sum_I [\hat{V}_I, \hat{\rho}_{RS}^i(t_0)] \int_{t_0}^t dt' e^{i\Omega_J(t'-t_0)} \\ & - \frac{1}{\hbar^2} \sum_{JK} [\hat{V}_J, [\hat{V}_K, \hat{\rho}_{RS}^i(t_0)]] \int_{t_0}^t dt' \int_{t_0}^{t'} dt'' e^{i\Omega_J(t'-t_0)} e^{i\Omega_K(t''-t_0)} \end{aligned} \quad (3-15)$$

Evaluation of the integrals over time requires a two-dimensional time-coordinate transformation. Let the first part of the time interval, $t'-t_0$, be given by

$$\xi = t''-t_0, \quad (3-16)$$

and the second part by

$$\tau = t'-t'' . \quad (3-17)$$

The area Jacobian is unity, i.e.,

$$dt'dt'' = d\tau d\xi . \quad (3-18)$$

After determination of the new limits of integration, Eq. (3-15) can be written

$$\begin{aligned} \hat{\rho}_{RS}^i(t) &= \hat{\rho}_{RS}^i(t_0) + \frac{1}{i\hbar} \sum_I \left[\hat{V}_I, \hat{\rho}_{RS}^i(t_0) \right] \\ &\int_0^{t-t_0} d\chi e^{i\Omega_I\chi} - \frac{1}{\hbar^2} \sum_{JK} \left[\hat{V}_J, \left[\hat{V}_K, \hat{\rho}_{RS}^i(t_0) \right] \right] \\ &\int_0^{t-t_0} d\xi e^{i(\Omega_K+\Omega_J)\xi} \int_0^{t-t_0-\xi} d\tau e^{i\Omega_J\tau} . \end{aligned} \quad (3-19)$$

The integral over τ must be completed first. Unless the eigenenergies $\epsilon_{i\alpha}$ which comprise Ω_J are all equal to zero, the integrand is the sum of many oscillating terms which tend to cancel each other except near $\tau = 0$. This fact suggests that the upper limit can be extended to

infinity with small error in the integration if we impose the condition

$$t_c \ll t - t_0, \quad (3-20)$$

where t_c is the correlation time. This condition allows us to write the integral over ξ as

$$\int_0^{t-t_0} d\xi e^{i(\Omega_K + \Omega_J)\xi} = (t-t_0) \delta_{\Omega_K, -\Omega_J}. \quad (3-21)$$

Use of Kronecker delta is meant to imply that the integral is zero unless Ω_K is identical to $-\Omega_J$. We cannot allow the upper limit of integration over χ to go to infinity and simultaneously maintain a dependence on τ in the second term; hence, the form of Eq. (3-21) must be used, i.e.,

$$\int_0^{t-t_0} d\chi e^{i\Omega_I\chi} = (t-t_0) \delta_{\Omega_I, 0} = 0. \quad (3-22)$$

The second step occurs because we have assumed that Ω_I is not identical to a set of zeros. If we define

$$\Delta \hat{\rho}_{RS}^i(t) = \hat{\rho}_{RS}^i(t) - \hat{\rho}_{RS}^i(t_0) \quad (3-23)$$

and

$$\Delta t = t - t_0, \quad (3-24)$$

the extension of the upper limit of integration over τ to infinity plus substitution of Eqs. (3-22) through (3-24) into Eq. (3-19) produces a finite difference equation for $\rho_{RS}^i(t)$:

$$\frac{\hat{\Delta}\rho_{RS}^i(\tau)}{\Delta t} = -\frac{1}{\hbar^2} \sum_{JK} \delta_{\Omega_J, -\Omega_K} \left[\hat{V}_J, \left[\hat{V}_K, \hat{\rho}_{RS}^i(t_0) \right] \right] \int_0^\infty d\tau e^{i\Omega_J \tau}. \quad (3-25)$$

The method of finding Ω_J and Ω_K from the form of $\hat{V}_J$ and $\hat{V}_K$ is given in Appendix II. From Eqs. (II-9) and (II-16) for $\hat{Q}_J$ and $\hat{F}_J$, respectively, it can be seen that this method implies that the Kronecker delta in the above equation is satisfied if $\hat{V}_K = \hat{V}_J^\dagger$ or $\hat{V}_J = \hat{V}_K^\dagger$. Summation over K leaves two terms corresponding to $\pm\Omega_J$,

$$\begin{aligned} \frac{\hat{\Delta}\rho_{RS}^i(\tau)}{\Delta t} = & -\frac{1}{\hbar^2} \sum_J \left\{ \left[\hat{V}_J, \left[\hat{V}_J^\dagger, \hat{\rho}_{RS}^i(t_0) \right] \right] \int_0^\infty d\tau e^{i\Omega_J \tau} \right. \\ & \left. + \left[\hat{V}_J^\dagger, \left[\hat{V}_J, \hat{\rho}_{RS}^i(t_0) \right] \right] \int_{-\infty}^0 d\tau e^{i\Omega_J \tau} \right\}. \end{aligned} \quad (3-26)$$

Restrictions on the time interval given by Eqs. (3-11) and (3-20) can be combined with Eq. (3-24) to give the restriction on Δt ,

$$t_c \ll \Delta t \ll \gamma^{-1}. \quad (3-27)$$

The required size of Δt in comparison to the density operator damping time suggests that we may take

$$\hat{\rho}_{RS}^i(t_0) \approx \hat{\rho}_{RS}^i(t) \quad (3-28)$$

in the right-hand side of Eq. (3-26). Because the correlation time t_c is expected to be very short (due to the expected large magnitude of eigenenergies for single-particle states), the condition specified by Eq. (3-27) can be fulfilled and Δt can be taken small enough to allow the approximation,

$$\frac{\partial \hat{\rho}_{RS}^i(t)}{\partial t} \approx \frac{\Delta \hat{\rho}_{RS}^i(t)}{\Delta t} \quad . \quad (3-29)$$

Using the approximations given by Eqs. (3-28) and (3-29) in Eq. (3-26) yields a differential equation for $\rho_{RS}^i(t)$,

$$\begin{aligned} \frac{\partial \hat{\rho}_{RS}^i(t)}{\partial t} = & -\frac{1}{\hbar^2} \sum_J \left\{ \left[\hat{V}_J, \left[\hat{V}_J^\dagger, \hat{\rho}_{RS}^i(t) \right] \right] \int_0^\infty d\tau e^{i\Omega_J \tau} \right. \\ & \left. + \left[\hat{V}_J^\dagger, \left[\hat{V}_J, \hat{\rho}_{RS}^i(t) \right] \right] \int_{-\infty}^0 d\tau e^{i\Omega_J \tau} \right\} \quad . \quad (3-30) \end{aligned}$$

If we take the trace of Eq. (3-1) over the reservoir and then over the system, we obtain two coupled differential equations. Before doing this, we can define:

$$\hat{H}_O = \hat{H}_C + \hat{H}_S + \hat{H}_R \quad , \quad (3-31)$$

and

$$\hat{V} = \sum_J \hat{V}_J \quad , \quad (3-32)$$

where $\hat{H}_C$ is the single-particle Hamiltonian common to both the reservoir and the system, $\hat{H}_S$ is the single-particle Hamiltonian acting on system states only, and $\hat{H}_R$ is the single-particle Hamiltonian acting on reservoir states only. The common term is allowed because single-particle Hamiltonians expanded in terms of creation and annihilation operators may be defined in the space of both system and reservoir states. By taking traces of Eq. (3-1), using Eqs. (2-23), (3-31), (3-32); and the Hermitian property of the single-particle state Hamiltonian operators we obtain the following two equations,

$$\frac{\partial \hat{\rho}_R^S(t)}{\partial t} = -\frac{1}{i\hbar} \left[\hat{\rho}_R^S(t), \hat{H}_R \right] - \frac{1}{i\hbar} \text{tr}_S \left[\hat{V}, \hat{\rho}_{RS}^S(t) \right] , \quad (3-33)$$

and

$$\frac{\partial \hat{\rho}_S^S(t)}{\partial t} = -\frac{1}{i\hbar} \left[\hat{\rho}_S^S(t), \hat{H}_S \right] - \frac{1}{i\hbar} \text{tr}_R \left[\hat{V}, \hat{\rho}_{RS}^S(t) \right] . \quad (3-34)$$

From these equations it can easily be seen that if there is no interaction ($\hat{V} = 0$), the equations uncouple. Lax (1964) shows that if we write the density operator as

$$\hat{\rho}_{RS}^S(t) = \hat{\rho}_R^S(t) \hat{\rho}_S^S(t) + \delta \hat{\rho}^S(t) , \quad (3-35)$$

and make the Hartree approximation (i.e., set $\delta \hat{\rho}^S(t) = 0$) Eqs. (3-33) and (3-34) again uncouple. This implies that $\delta \hat{\rho}^S(t)$ is of order $\hat{V}$; hence, Eq. (3-35) can be written in the interaction picture as

$$\hat{\rho}_{RS}^i(t) = \hat{\rho}_R^i(t) \hat{\rho}_S^i(t) + O(\hat{V}) \quad (3-36)$$

Substitution of Eq. (3-36) into the right-hand side of Eq. (3-30) reveals that the term $\delta\hat{\rho}^s(t)$ in Eq. (3-35) generates a term that is of third order in $\hat{V}$ in an expansion that was terminated at second order; hence, the Hartree approximation in Eq. (3-30) is justified.

We are now able to obtain an equation of motion in the Schrödinger picture. After making the Hartree approximation in Eq. (3-30); substituting the result into Eq. (3-9); using Eq. (3-5) for $\hat{U}(t, t_0)$, Eq. (3-7) for $\hat{V}(t-t_0)$, Eq. (3-6) for $\hat{\rho}_{RS}^s(t)$; and employing Eq. (3-14) we find that

$$\begin{aligned} \frac{\partial \hat{\rho}_{RS}^s(t)}{\partial t} = & -\frac{1}{i\hbar} [\hat{\rho}_{RS}^s(t), \hat{H}_0] \\ & - \frac{1}{\hbar^2} \sum_J \left\{ \left[\hat{V}_J, \left[\hat{V}_J^\dagger, \hat{\rho}_R^s(t) \hat{\rho}_S^s(t) \right] \right] \int_0^\infty d\tau e^{i\Omega_J \tau} \right. \\ & \left. + \left[\hat{V}_J^\dagger, \left[\hat{V}_J, \hat{\rho}_R^s(t) \hat{\rho}_S^s(t) \right] \right] \int_{-\infty}^0 d\tau e^{i\Omega_J \tau} \right\}. \quad (3-37) \end{aligned}$$

This equation of motion implies that the time rate of change of the density operator depends only on the current state of the system, i.e., memory effects have been removed. An equation of motion of this type is generally referred to as a Markoff approximation. The removal of memory effects is a consequence of the approximations implied by Eqs. (3-12) and (3-28) plus the extension of the upper limit over τ in Eq. (3-19)

to infinity. These approximations are valid when Eq. (3-27) is valid. The Markoff approximation is invalid if the correlation time is a significant fraction of the characteristic time for system evolution.

Up to this point we have been considering a composite system consisting of two parts, a reservoir and a system; however, we have not assigned any unique features to either. For most physical situations the composite system will consist of sets of mixed states (composed of pure states), which are interacting with sets of pure states. The problem of interest is to find the distribution of single-particle states we shall consider pure states. We do this by considering the reservoir a set of mixed states and by taking the trace of Eq. (3-37) over the reservoir to eliminate this unwanted part of the density operator. The implications are that the system will be in Hilbert space $H^{(1)}$ and that reservoir will be in Fock space F ; and that the trace over the reservoir must be done in the number representation. The interaction operator of Eq. (3-13) is defined so that $\hat{Q}_J$ is in $H^{(1)}$ and $\hat{F}_J$ is in F ; hence, $\hat{Q}_J$ is considered to be a system term and $\hat{F}_J$ a reservoir term. Let us assume that $\hat{V}_J$ can be written so that $\hat{F}_J$ and $\hat{Q}_J$ commute, i.e.,

$$[\hat{F}_J, \hat{Q}_J] = 0, \quad (3-38)$$

and define

$$\langle \hat{F}_J^\dagger \hat{F}_J \rangle \equiv \text{tr}_R \left(\hat{\rho}_R^s(t) \hat{F}_J^\dagger \hat{F}_J \right). \quad (3-39)$$

Then, by taking the trace of Eq. (3-37) over the reservoir, and by using Eqs. (3-13), (3-38), and (3-39) plus some of the techniques

leading to Eq. (3-34), we find the master equation for the system density operator:

$$\begin{aligned}
\frac{\partial \hat{\rho}_{RS}(t)}{\partial t} = & -\frac{1}{i\hbar} \left[\hat{\rho}_S(t), \hat{H}_S \right] \\
& - \sum_J \left\{ \left[\hat{Q}_J, \hat{Q}_J^\dagger \hat{\rho}_S(t) \right] \int_0^\infty d\tau e^{i\Omega_J \tau} \right. \\
& + \left. \left[\hat{\rho}_S(t) \hat{Q}_J, \hat{Q}_J^\dagger \right] \int_{-\infty}^0 d\tau e^{i\Omega_J \tau} \right\} \langle \hat{F}_J \hat{F}_J^\dagger \rangle \\
& - \sum_J \left\{ \left[\hat{\rho}_S(t) \hat{Q}_J^\dagger, \hat{Q}_J \right] \int_0^\infty d\tau e^{i\Omega_J \tau} \right. \\
& + \left. \left[\hat{Q}_J^\dagger, \hat{Q}_J \hat{\rho}_S(t) \right] \int_{-\infty}^0 d\tau e^{i\Omega_J \tau} \right\} \langle \hat{F}_J^\dagger \hat{F}_J \rangle. \quad (3-40)
\end{aligned}$$

All further analysis will be in the Schrödinger picture; we have, therefore, omitted the s superscript.

Except for differences in notation that arise from the use of Appendix II, the above master equation is identical to the master equation derived by Louisell (1973, Eq. 6.2.35). Our derivation, however, uses a Hamiltonian $\hat{H}_0$ that can have terms defined in both the system and the reservoir space. This property is important in application to nucleation theory because reservoir states contain combinations of system (single-particle) states. Additionally, our master equation defines limitations on the system operator $\hat{Q}_J$ and offers a simplified method of finding Ω_J . Also, we eliminated the requirement that the reservoir Hamiltonian $\hat{H}_C + \hat{H}_R$ commute with the reservoir density operator $\hat{\rho}_R$.

The operator $\hat{\rho}_S(t)$ is the density operator for all the single-particle states. To find the probability of a given state, we take the scalar product of Eq. (3-40) with single-particle state vectors. It can be shown that this procedure is appropriate by noting that for pure states

$$\hat{\rho}_S(t) = | \psi_S(q,t) \rangle \langle \psi_S(q,t) | , \quad (3-41)$$

as implied by Eq. (2-6). Taking the scalar product of Eq. (3-41) with the vector $|i\alpha\rangle$ and its adjoint, and using Eq. (2-66), indicates that the probability is given by

$$P_{i\alpha}(t) = | \psi_{i\alpha}(q,t) |^2 = \langle i\alpha | \hat{\rho}_S(t) | i\alpha \rangle . \quad (3-42)$$

Note that the second commutator in Eq. (3-40) is the Hermitian adjoint of the third, and that the fourth and fifth commutators are also adjoint. If we take the scalar product of Eq. (3-40) with $|i\alpha\rangle$ and its adjoint, the second term combines with the third and the fourth term with the fifth. By using the definition of the delta function,

$$\delta(x) = 2\pi \int_{-\infty}^{\infty} d\tau e^{ix\tau} , \quad (3-43)$$

the preceding conclusion, and Eq. (3-42), we find that the scalar product of Eq. (3-40) produces the following master equation for the probability of existence of the $i(\alpha)^{\text{th}}$ energy state:

$$\begin{aligned} \frac{\partial P_{i\alpha}(\tau)}{\partial \tau} = 2\pi \sum_J \delta(\Omega_J) \left\{ \langle i\alpha | \left[\hat{Q}_J^\dagger \hat{\rho}_S(\tau), \hat{Q}_J \right] | i\alpha \rangle \left\langle \hat{F}_J \hat{F}_J^\dagger \right\rangle \right. \\ \left. + \langle i\alpha | \left[\hat{Q}_J \hat{\rho}_S, \hat{Q}_J^\dagger \right] | i\alpha \rangle \left\langle \hat{F}_J^\dagger \hat{F}_J \right\rangle \right\} . \quad (3-44) \end{aligned}$$

This general master equation can be applied to problems that involve systems interacting with a reservoir and that have Hamiltonians expressible as functions of creation and annihilation operators. In Ch. 4 we will consider the eigenstates of molecular clusters as single-particle states and will use Eq. (3-44) to obtain time-dependent probabilities for the formation of clusters of various sizes in the nucleation process.

Although the master equation, Eq. (3-40), is similar to rate equations from second-order perturbation theory, there is one physical difference of great importance, as observed by Louisell and Marmburger (1967): perturbation theory is incapable of yielding exponential decay, but the master equation reservoir provides this capability by acting as a damping mechanism. The role of reservoir correlation functions as a damping mechanism is illustrated by the fluctuation-dissipation theorem applied to Brownian motion by Sargent, Scully, and Lamb (1974, Ch. 19).

CHAPTER 4

MASTER EQUATION FOR NUCLEATION

A master equation for a system in contact with a thermal reservoir was developed in Ch. 3. This equation, Eq. (3-44), describes the time evolution of the probability of each energy level in terms of an interaction operator. In this chapter we shall define the interaction operator as a function of creation and annihilation operators, which model the process of homogeneous nucleation. We assume that the nucleation process consists of (1) scatterings of clusters with carrier-gas molecules, which result in energy exchanges only, and (2) interaction between clusters that result in changes in cluster size. The interaction operator is defined by system and reservoir factors, and the matrix elements required by Eq. (3-44) are evaluated. A steady-state solution of the scattering part of the master equation is found. This solution is a distribution function of energy levels in the form of the grand canonical ensemble with a different chemical potential for each cluster size. The physical meaning of certain coefficients is determined by comparison with the Euler relation of thermodynamics. The steady-state solution of the scattering part of the master equation is substituted in the remaining part of the master equation, which describes cluster growth and evaporation to obtain the final form. Transition rates for growth and evaporation are defined, which permit us to write the master equation in much more compact form. Finally, the master equation is transformed into a Pauli master equation with unsymmetrical transition coefficients.

The master equations presented in this chapter are the result of a complete derivation from many-body quantum mechanics. The only approximation

required for the development of the complete master equation that describes both cluster growth and scattering is the Markoff approximation. This approximation is valid whenever the system response time is long compared to the interaction time. An additional approximation occurs when we use the steady-state solution of the scattering part of the complete master equation to obtain a cluster growth master equation. This approximation is valid for most experiments because the ratio of number density of carrier-gas molecules to the number density of condensing molecules is usually large. As a consequence of this derivation all parts of the master equation are functions of eigenenergies and eigenvectors, which are defined by a particular set of basis vectors. Given a set of eigenenergies, determined either from solutions of the single-particle Schrödinger equation or by a full set of state-to-state scattering cross sections, the required free energies and kinetic coefficients (up and down) can, in principle, be determined ab initio. In our approach it is neither necessary to assume a relation between the kinetic coefficients from statistical mechanics nor to introduce an absorption cross section from kinetic theory. Also, the equilibrium and steady-state distributions are derived results rather than ad hoc solutions introduced either as part of the development or from a statistical-mechanics technique that uses the maximum-entropy principle. The change from a reversible quantum mechanics description to the irreversible master equation is a consequence of applying the Markoff approximation; hence, statistical mechanics enters the development when this approximation is introduced.

A dynamic system of clusters can (1) change in its distribution of cluster sizes by adding monomers to the clusters and by coalescence of

clusters, or (2) change its energy levels by collisions with carrier-gas molecules (which can be at a much higher density than the clusters). Other processes, e.g., elastic collisions between clusters are not as important and will be disregarded. An external source term, e.g., laser pumping of specific energy levels has not been included. Hence, the interaction operator is the sum of two parts:

$$\hat{V} = \hat{V}^{(1)} + \hat{V}^{(2)} \quad (4-1)$$

The first part, which represents cluster growth, is

$$\hat{V}^{(1)} = \hbar \sum_{i\alpha j\beta k\gamma} \delta_{\alpha, \beta+\gamma} \omega_{i\alpha j\beta k\gamma} a_{i\alpha}^{\dagger} a_{j\beta} b_{k\gamma} \quad (4-2)$$

In the above equation, $b_{i\alpha}$ annihilates the $i(\alpha)^{\text{th}}$ energy state of a cluster of α molecules when it operates on a reservoir ket we consider in Fock space, F . The operator, $a_{j\beta}$, annihilates the $j(\beta)^{\text{th}}$ system state for a cluster of β molecules and $a_{i\alpha}^{\dagger}$ creates a system state for a cluster of $\alpha = \beta + \gamma$ molecules. We will consider the system states to be in the single-particle Hilbert space $H^{(1)}$. Molecule conservation is ensured by the delta function. The factor $\omega_{i\alpha j\beta k\gamma}$ is an expansion coefficient, which can be determined from scalar products of the Hamiltonian operator. The sum over Greek subscripts is restricted to numbers in the domain of positive integers. Bearing in mind the development of App. II and Eq. (3-13), the system part of the interaction operator is

$$\hat{Q}_J = \delta_{\alpha, \beta+\gamma} a_{i\alpha}^{\dagger} a_{j\beta} \quad (4-3)$$

the reservoir part is

$$\hat{F}_J = \omega_{i\alpha j\beta k\gamma} b_{k\gamma} \quad , \quad (4-4)$$

the sum over the set of quantum numbers implied by Σ_J is

$$\sum_J = \sum_{i\alpha j\beta k\gamma} \quad , \quad (4-5)$$

and the argument of the delta function in Eq. (3-44) is, by inspection of Eq. (4-2),

$$\Omega_J = \omega_{i\alpha} - \omega_{j\beta} - \omega_{k\gamma} \quad . \quad (4-6)$$

System and reservoir terms commute because $\alpha = \beta$ and $\alpha = \gamma$ do not occur. The Hermitian adjoint of Eq. (4-2) represents a decrease in clusters of α molecules by evaporation of monomers, or, possibly, by fission processes.

Equations (4-3) and (4-4) can be directly substituted into Eq. (3-44) and the required matrix elements and reservoir traces can easily be obtained. With the assistance of Eqs. (2-32), (2-33), and (3-44), a sample matrix element is found to be

$$\begin{aligned} & \langle m\delta | \left[\hat{Q}_J^\dagger \hat{\rho}_S(t), \hat{Q}_J \right] | m\delta \rangle \\ &= \delta_{\alpha, \beta+\gamma} \left(\delta_{jm} \delta_{\beta\delta} - \delta_{im} \delta_{\alpha\delta} \right) P_{i\alpha}(t) \quad . \end{aligned} \quad (4-7)$$

Equations (2-48) and (2-52) can be employed to show that a sample reservoir term can be written as

$$\begin{aligned} \langle \hat{F}_J^\dagger \hat{F}_J \rangle &= | \omega_{i\alpha j\beta k\gamma} |^2 \langle b_{k\gamma} b_{k\gamma}^\dagger \rangle_R \\ &= | \omega_{i\alpha j\beta k\gamma} |^2 \left(\bar{n}_{k\gamma}(t) + 1 \right) , \end{aligned} \quad (4-8)$$

where we defined

$$\bar{n}_{k\gamma}(t) = \langle \hat{n}_{k\gamma} \rangle_R \quad (4-9)$$

as the average number of clusters of γ molecules in the $k(\gamma)^{th}$ energy level. The average number is written as a function of time because we are in the Schrödinger picture where the state vectors are functions of time. Evaluation of the remaining terms, their substitution into Eq. (3-44), and use of Eq. (4-5) for Σ_J and of Eq. (4-6) for Ω_J lead to the following master equations for cluster growth and evaporation,

$$\begin{aligned} -\frac{\partial P_m^{(1)}(t)}{\partial t} &= 2\pi \sum_{i\alpha j\beta k\gamma} \delta(\omega_{i\alpha} - \omega_{j\beta} - \omega_{k\gamma}) | \omega_{i\alpha j\beta k\gamma} |^2 \delta_{\alpha, \beta+\gamma} \\ & \left\{ P_{i\alpha}(t) \left(\bar{n}_{k\gamma}(t) + 1 \right) - P_{j\beta}(t) \bar{n}_{k\gamma}(t) \right\} . \end{aligned} \quad (4-10)$$

After summation over α , β , and i or j the above master equation becomes

$$\begin{aligned}
\frac{\partial P_{m\delta}^{(1)}(t)}{\partial t} = & 2\pi \sum_{\gamma=1}^{\infty} \sum_{ik} \delta(\omega_{i(\gamma+\delta)} - \omega_{m\delta} - \omega_{k\gamma}) \\
& \left| \omega_{i(\delta+\gamma)m\delta k\gamma} \right|^2 \left\{ P_{i(\delta+\gamma)}(t) \left(\bar{n}_{k\gamma}(t) + 1 \right) - P_{m\delta}(t) \bar{n}_{k\gamma}(t) \right\} \\
& + 2\pi \sum_{\gamma=1}^{\delta-1} \sum_{jk} \delta(\omega_{m\delta} - \omega_{j(\delta-\gamma)} - \omega_{k\gamma}) \left| \omega_{m\delta j(\delta-\gamma)k\gamma} \right|^2 \\
& \left\{ P_{j(\delta-\gamma)}(t) \bar{n}_{k\gamma}(t) - P_{m\delta}(t) \left(\bar{n}_{k\gamma}(t) + 1 \right) \right\} . \quad (4-11)
\end{aligned}$$

For cluster energy changes caused by scatterings with carrier-gas molecules, we define the following interaction operator

$$\hat{V}^{(2)} = \kappa \sum_{ij\alpha k\ell} (1 - \delta_{ij}) \omega_{i\alpha j\alpha k\ell} a_{i\alpha}^{\dagger} d_k^{\dagger} a_{j\alpha} d_{\ell} . \quad (4-12)$$

For this interaction $d_k^{\dagger}$ and d_{ℓ} are creation and annihilation operators in the Fock space of the carrier gas which is considered to be the reservoir part of the interaction. The cluster size of the carrier gas is not specified because it is assumed that the temperature and volume are such that the carrier gas will not condense. The operators $a_{i\alpha}^{\dagger}$ and $a_{j\alpha}$ are defined as in the cluster growth operator. The expansion coefficient is $\omega_{i\alpha j\alpha k\ell}$ and the term $(1 - \delta_{ij})$ prevents interactions with no energy change. The system and reservoir operators commute because they represent

different kinds of particles. Appendix II and Eq. (3-13) allow us to define the system part of the interaction operator as

$$\hat{Q}_J = (1 - \delta_{ij}) a_{i\alpha}^\dagger a_{j\alpha} \quad , \quad (4-13)$$

the reservoir part as

$$\hat{F}_J = \omega_{i\alpha j\alpha k\ell} d_k^\dagger d_\ell \quad , \quad (4-14)$$

the sum over the set of quantum numbers implied by Σ_J as

$$\Sigma_J = \sum_{i\alpha j\alpha k\ell} \quad , \quad (4-15)$$

and the argument of the delta function in Eq. (3-44) [by inspection of Eq. (4-12)] as

$$\Omega_J = \omega_{i\alpha} - \omega_{j\alpha} + \omega_k - \omega_\ell \quad . \quad (4-16)$$

The matrix elements and reservoir traces required by Eq. (3-44) have been evaluated by using Eqs. (4-13) and (4-14). After substituting these results and Eqs. (4-15) and (4-16) into Eq. (3-44) the scattering master equation for changes in energy levels is

$$\frac{\partial P_{m\delta}^{(2)}(t)}{\partial t} = 2\pi \sum_{ij\alpha k\ell} (1 - \delta_{ij}) |\omega_{i\alpha j\alpha k\ell}|^2 \delta_{\alpha\delta}$$

$$\begin{aligned} & \delta(\omega_{i\alpha} - \omega_{j\alpha} + \omega_k - \omega_\ell) \left\{ \delta_{mj} \left(P_{i\alpha}(t) \bar{n}_k(t) (\bar{n}_\ell(t) + 1) \right. \right. \\ & - P_{j\alpha}(t) \bar{n}_\ell(t) (\bar{n}_k(t) + 1) \left. \left. \right) + \delta_{mi} \left(P_{j\alpha}(t) \bar{n}_\ell(t) (\bar{n}_k(t) + 1) \right. \right. \\ & - P_{i\alpha}(t) \bar{n}_k(t) (\bar{n}_\ell(t) + 1) \left. \left. \right) \right\} . \end{aligned} \quad (4-17)$$

The sum over α and i or j can be completed; the symmetry property of the delta function, $\delta(x) = \delta(-x)$, can be employed; and the symmetry of k and ℓ under the double sum can be used to write the master equation, Eq. (4-17), as

$$\begin{aligned} \frac{\partial P_{m\delta}^{(2)}(t)}{\partial t} &= 2\pi \sum_{i\alpha k\ell} (1 - \delta_{im}) \left[|\omega_{i\delta m\delta k\ell}|^2 + |\omega_{m\delta i\delta \ell k}|^2 \right] \\ & \delta(\omega_{i\delta} - \omega_{m\delta} + \omega_k - \omega_\ell) \left\{ P_{i\delta}(t) \bar{n}_k(t) (\bar{n}_\ell(t) + 1) \right. \\ & - P_{m\delta}(t) \bar{n}_\ell(t) (\bar{n}_k(t) + 1) \left. \right\} . \end{aligned} \quad (4-18)$$

Because the interaction potential, Eq. (4-1), is the sum of two terms defined by Eqs. (4-2) and (4-12), we can write the master equation for energy level changes as the sum of two terms,

$$\frac{\partial P_{m\delta}(t)}{\partial t} = -\frac{\partial P_{m\delta}^{(1)}(t)}{\partial t} + \frac{\partial P_{m\delta}^{(2)}(t)}{\partial t} \quad (4-19)$$

The first term is the time rate of change of probabilities of energy levels that are a consequence of the interaction operator $\hat{V}^{(1)}$ in Eq. (4-1). Physically, it represents changes in energy levels that result from collisions between clusters leading to coalescence of two clusters. This term is given mathematically by Eq. (4-11). The second term, which we call the scattering term, is the time rate of change of probability of energy levels that are a consequence of the interaction operator $\hat{V}^{(2)}$ in Eq. (4-1). Physically, this term represents collisions between clusters and carrier-gas molecules or, possibly, collisions between clusters when no coalescence occurs. It is given mathematically by Eq. (4-18).

A steady-state solution of the scattering term is

$$\frac{\partial P_{m\delta}^{(2)}(t)}{\partial t} = 0 \quad (4-20)$$

Conditions where this steady-state solution is valid are attained in most nucleation experiments by keeping the carrier gas at a much higher density than the condensing gas. The coefficients of terms in braces {} in Eq. (4-18) are linearly independent; hence, a steady-state solution is given by

$$\frac{P_{i\delta}(t)}{P_{m\delta}(t)} = \frac{\tilde{n}_{l\beta}(t)}{\tilde{n}_{k\beta}(t)} \quad (4-21)$$

where we defined

$$\tilde{n}_{\ell\beta}(t) = \frac{\bar{n}_{\ell\beta}(t)}{1 + \bar{n}_{\ell\beta}(t)} \quad . \quad (4-22)$$

Equation (4-21) is written as a function of time because the steady-state condition, Eq. (4-20), does not imply complete equilibrium in Eq. (4-19). The subscript β has been added to identify the reservoir term. The delta function in Eq. (4-18) applies to the term in the brackets if the system has the smallest imaginable deviation from steady state; hence, we assume it also applies in the steady state. This implies that, in addition to Eq. (4-21), another equation is applicable to the steady state, which we get from the delta function and Eq. (2-58):

$$\epsilon_{i\delta} - \epsilon_{m\delta} = \epsilon_{\ell\beta} - \epsilon_{k\beta} \quad . \quad (4-23)$$

The logarithm of both sides of Eq. (4-21) leaves the steady-state solution in the form

$$\ln P_{i\delta}(t) - \ln P_{m\delta}(t) = \ln \tilde{n}_{\ell\beta}(t) - \ln \tilde{n}_{k\beta}(t) \quad . \quad (4-24)$$

When calculating $\bar{n}_{k\gamma}(t)$ by Eq. (4-9), it is easily shown that the result depends only on the ket vectors $|n_{k\gamma}\rangle$. In the number representation the kets $|n_{k\gamma}\rangle$ depend only on eigenenergies $\epsilon_{k\gamma}$; therefore, the $\bar{n}_{k\gamma}(t)$ depend only on $\epsilon_{k\gamma}$. Similarly the $P_{i\delta}(t)$ depend only on $\epsilon_{i\delta}$. We expand each of the terms in Eq. (4-24) in a power series in the eigenenergies:

$$\ln \tilde{n}_{\ell\beta}(t) = \sum_p \left[c_{\beta}(t) \right]_p \epsilon_{\ell\beta}^p \quad , \quad (4-25)$$

$$\ln P_{i\delta}(t) = \sum_p \left[z_{\delta}(t) \right]_p \epsilon_{i\delta}^p. \quad (4-26)$$

The eigenenergies are solutions of the time-independent Schrödinger equation; hence, the time dependence is contained in the expansion coefficients. To determine the expansion coefficients, we substitute Eqs. (4-25), (4-26), and (4-23) into Eq. (4-24) and equate coefficients of various powers of $\epsilon_{i\alpha}$ to zero. These coefficients are zero because the eigenenergies are linearly independent; i.e., the kets $|i\alpha\rangle$ are basis vectors in $H^{(1)}$. This analysis leads to the conditions:

$$\left[c_{\delta}(t) \right]_2 = \left[c_{\beta}(t) \right]_2 = B(t), \quad (4-27)$$

and

$$\left[c_{\delta}(t) \right]_p = \left[c_{\beta}(t) \right]_p = 0, \quad p \geq 3. \quad (4-28)$$

Substitution of Eqs. (4-27) and (4-28) into Eq. (4-25) yields the functional form

$$\tilde{n}_{\ell\beta}(t) = e^{\left(\left[c_{\beta}(t) \right]_1 + B(t) \epsilon_{\ell\beta} \right)}. \quad (4-29)$$

The probability has the same form, i.e.,

$$P_{i\alpha}(t) \propto \tilde{n}_{i\alpha}(t). \quad (4-30)$$

The terms $c_{\beta}(t)$ and $B(t)$ can be redefined in terms of two other functions,

$$\Theta(t) = \frac{1}{B(t)} \quad \text{and} \quad \chi_{\alpha}(t) = \Theta(t) \left[c_{\alpha}(t) \right]_1 ,$$

and Eq. (4-29) can be substituted into Eq. (4-22) to obtain the number distribution function in a familiar form:

$$\bar{n}_{i\alpha}(t) = \frac{e^{(\epsilon_{i\alpha} + \chi_{\alpha}(t))/\Theta(t)}}{1 - e^{(\epsilon_{i\alpha} + \chi_{\alpha}(t))/\Theta(t)}} . \quad (4-31)$$

Note that Eq. (4-30) makes Eq. (4-31) applicable to both, system and reservoir, states.

The distribution function, Eq. (4-31), can be used to determine properties of the total system, and hence the functions χ_{α} and Θ can be related to these properties. The energy, in the representation in which the operator $\hat{H}_O$ is diagonal, is

$$E_O = \langle \hat{H}_O \rangle_R = \text{tr}_R \langle \hat{c}_R \hat{H}_O \rangle . \quad (4-32)$$

To find E_O in terms of the distribution function, we use Eqs. (2-59) for $\hat{H}_O$, Eq. (2-48) for $\hat{n}_{i\alpha}$, and the definition, Eq. (4-9). The result is

$$E_O(t) = \sum_{i\alpha} \epsilon_{i\alpha} \bar{n}_{i\alpha}(t) . \quad (4-33)$$

Additionally, the average number of clusters containing α molecules is

$$\bar{n}_{\alpha}(t) = \sum_i \bar{n}_{i\alpha}(t) . \quad (4-34)$$

Note that the Greek subscript could also be used to identify different chemical species. Because all variables except $\epsilon_{i\alpha}$ are functions of time, we temporarily drop the explicit time dependence. Equations (4-33) and (4-34) provide enough information to relate χ_α and Θ to macroscopic quantities. The form of Eq. (4-31) suggests that these relationships can be found in the form of differential equations if we define a potential function

$$\chi = \sum_{i\alpha} \ln \left(1 - e^{(\epsilon_{i\alpha} + \chi_\alpha)/\Theta} \right) . \quad (4-35)$$

From Eqs. (4-33) through (4-35) the total energy is

$$E_o = - \frac{\partial \chi}{\partial \left(\frac{1}{\Theta} \right)} - \sum_{\alpha} \chi_{\alpha} \bar{n}_{\alpha} , \quad (4-36)$$

and the average number of clusters containing α molecules is

$$\bar{n}_{\alpha} = - \Theta \frac{\partial \chi}{\partial \chi_{\alpha}} . \quad (4-37)$$

The quantities E_o and $\bar{n}_{\alpha}$ are also related by differential equations in thermodynamics. To find an equation similar to Eq. (4-36), we start with the Euler equation as given by Callen (1960, p. 115):

$$S/T = E/T + P/V - \sum_{\alpha} G_{\alpha} \bar{n}_{\alpha} , \quad (4-38)$$

where S is the entropy, T is the temperature, P is the pressure, V is the volume, $\bar{n}_{\alpha}$ is the number of a given species, G_{α} is the Gibbs free

energy per particle, and E is the internal energy. Differentiation of Eq. (4-38) yields

$$-\left(\frac{\partial\left(\frac{PV}{T}\right)}{\partial\left(\frac{1}{T}\right)}\right)_{SVG_{\alpha}} = E - \sum_{\alpha} G_{\alpha} \bar{n}_{\alpha} \quad (4-39)$$

Comparison of Eqs. (4-36) and (4-39) reveals that the steady-state solution of the scattering master equation follows the laws of thermodynamics, along an isentrope, if we take

$$G = a/T \quad , \quad (4-40)$$

$$\chi = \frac{PV}{aT} \quad , \quad (4-41)$$

and

$$\chi_{\alpha} = -G_{\alpha} \quad . \quad (4-42)$$

Furthermore, we can relate E_0 , P/V , and $G_{\alpha} \bar{n}_{\alpha}$ by taking weighted sums of logarithms of Eq. (4-31) and using Eqs. (4-31), (4-35), (4-40), and (4-41) to obtain

$$\begin{aligned} & a/T \sum_{i\alpha} \left\{ \bar{n}_{i\alpha} \ln \bar{n}_{i\alpha} - (1 + \bar{n}_{i\alpha}) \ln (1 + \bar{n}_{i\alpha}) \right\} \\ & = E + PV - \sum_{\alpha} G_{\alpha} \bar{n}_{\alpha} \quad . \end{aligned} \quad (4-43)$$

Comparison of Eqs. (4-43) and (4-38) (the Euler equation), reveals that the result on the left-hand side of Eq. (4-43) is proportional to the quantity identified as the entropy. If we take $\beta = 1/kT$, the Boltzman constant, we get the equation for the entropy of bosons [Fetter and Walecka (1971)].

$$S = -k \sum_{i\alpha} \left\{ \bar{n}_{i\alpha} \ln \bar{n}_{i\alpha} + (1 + \bar{n}_{i\alpha}) \ln (1 + \bar{n}_{i\alpha}) \right\} . \quad (4-44)$$

Distribution functions in terms of thermodynamic variables are found by combining Eqs. (4-31), (4-40), and (4-42). The average number distribution is

$$\bar{n}_{i\alpha}(t) = \frac{e^{-(\epsilon_{i\alpha} - G_{\alpha})/kT}}{1 + e^{-(\epsilon_{i\alpha} - G_{\alpha})/kT}} . \quad (4-45)$$

Combining the above equation with Eq. (4-22) gives the probability-number distribution,

$$\tilde{n}_{i\alpha}(t) = e^{-(\epsilon_{i\alpha} - G_{\alpha})/kT} . \quad (4-46)$$

The thermodynamic potential calculated from Eqs. (4-35), (4-40) through (4-42), and (4-45) is

$$P/V = kT \sum_{i\alpha} \ln (1 + \bar{n}_{i\alpha}) . \quad (4-47)$$

Note that S and PV/T are both functions of the average number distribution only. The master equation distinguishes the quantity $S/T - P/V$ only from E_0 and $\sum_{\alpha} G_{\alpha} \bar{n}_{\alpha}$. To identify S/T and P/V as different terms,

two equations from thermodynamics are needed, i.e., the Euler equation, Eq. (4-36), and its differential at constant entropy, Eq. (4-39).

Given a set of energy levels $\epsilon_{i\alpha}$, from Schrödinger's equation, one can (in principle) sum over $i(\alpha)$ and α in Eq. (4-47) to obtain P/V . A complete set of equations-of-state formulas can then be obtained by differentiating Eq. (4-47), i.e., Eqs. (4-36), (4-37), and (4-38) can be employed. This procedure assumes a given set of Gibbs free energies, G_α . We will show that G_α is directly related to $\tilde{n}_\alpha$ and, hence, can be obtained as a function of time by solving the master equation for growth and evaporation of clusters. The Helmholtz free energy of a cluster can be defined as

$$F_\alpha(t) = -kT \ln \sum_i e^{-\epsilon_{i\alpha}/kT} \quad (4-48)$$

and $\tilde{n}_\alpha$ can be defined as

$$\tilde{n}_\alpha \equiv \sum_i \tilde{n}_{i\alpha} \quad (4-49)$$

Summing Eq. (4-46) over $i(\alpha)$ and using Eqs. (4-48) and (4-49) gives

$$\tilde{n}_\alpha = e^{-(F_\alpha - G_\alpha)/kT} \quad (4-50)$$

The time dependence in the above equation is contained in both the temperature, T , and in G_α . For a fixed temperature we find

$$G_\alpha(t) = F_\alpha + kT \ln \tilde{n}_\alpha(t) \quad ; \quad (4-51)$$

hence, G_α can change in time because the number of clusters is changing.

we can use Eq. (4-51) to show that the number in each energy level is changing, because the number of particles is changing when the temperature is at a fixed value. From Eqs. (4-46) and (4-51):

$$n_{i+1}(t) - n_{i\alpha}(t) = e^{-(\epsilon_{i+1} - \epsilon_{i\alpha})/kT} \quad (4-52)$$

We can use Eq. (4-36) to find a similar equation for the probability

$$P_{i+1}(t) - P_{i\alpha}(t) = e^{-(\epsilon_{i+1} - \epsilon_{i\alpha})/kT} \quad (4-53)$$

where

$$I_{i\alpha}(t) = \sum_1 P_{i\alpha}(t) \quad (4-54)$$

Substitution of Eqs. (4-52) and (4-53) into (4-18) after using Eq. (4-21) in Eq. (4-18) reveals that the steady-state solution of the scattering master equation is valid when the system and reservoir are at the same temperature. Time rates of change of the number of clusters of every size is allowed by the steady-state solution if the energy distribution of each cluster is given by a density of states

$$\rho_{i\alpha} \equiv e^{-(\epsilon_{i\alpha} - F_{\alpha})/kT} \quad (4-55)$$

For problems where the steady-state solution of the master equation is valid, we can obtain a master equation for cluster growth and evaporation by combining Eqs. (4-19), (4-20), and (4-11). Equations (4-52) and (4-53) can be substituted into the resultant equation; Eq. (2-58) can

be used; the delta function can be used; and the result summed over m to obtain

$$\begin{aligned}
 \frac{dP_{\delta}(t)}{dt} = & 2\pi \sum_{\gamma=1}^s \sum_{ikm} \delta(\omega_{i(\delta+\gamma)} - \omega_{m\delta} - \omega_{k\gamma}) \\
 & \left[\omega_{i(\delta+\gamma)m\delta k\gamma} \left(\bar{n}_{k\gamma}(t) + 1 \right) e^{-\left(\varepsilon_{m\delta} - F_{\delta}\right)/kT} e^{-\left(\varepsilon_{k\gamma} - F_{\gamma}\right)/kT} \right. \\
 & \left. \left\{ P_{i+\gamma}(t) e^{-\left(F_{\delta} + F_{\gamma} - F_{i+\gamma}\right)/kT} - P_{\delta}(t) \tilde{n}_{\gamma}(t) \right\} \right. \\
 & + 2\pi \sum_{\gamma=1}^{s-1} \sum_{ikm} \delta(\omega_{m\delta} - \omega_{i(\delta-\gamma)} - \omega_{k\gamma}) \left| \omega_{m\delta i(\delta-\gamma)k\gamma} \right|^2 \\
 & \left(\bar{n}_{k\gamma}(t) + 1 \right) e^{-\left(\varepsilon_{i(\delta-\gamma)} - F_{\delta-\gamma}\right)/kT} e^{-\left(\varepsilon_{k\gamma} - F_{\gamma}\right)/kT} \\
 & \left. \left\{ P_{\delta-\gamma}(t) \tilde{n}_{\gamma}(t) - P_{\delta}(t) e^{-\left(F_{\delta-\gamma} + F_{\gamma} - F_{\delta}\right)/kT} \right\} \right] . \quad (4-56)
 \end{aligned}$$

If we define a transition rate as

$$\begin{aligned}
 A_{\alpha,\beta} = & 2\pi \sum_{ijk} \delta(\omega_{i(\alpha+\beta)} - \omega_{j\alpha} - \omega_{k\beta}) \\
 & \left| \omega_{i(\alpha+\beta)j\alpha k\beta} \right|^2 \left(\bar{n}_{k\beta}(t) + 1 \right) \rho_{j\alpha} \rho_{k\beta} , \quad (4-57)
 \end{aligned}$$

and use Eq. (4-57) for the density of states, the master equation can be written more compactly as

$$\begin{aligned} \frac{d\bar{n}_{\delta+\gamma}}{dt} = & \sum_{\gamma=1}^{\infty} A_{\delta,\gamma} \left\{ \bar{n}_{\delta+\gamma}(t) e^{-(F_{\delta} + F_{\gamma} - F_{\delta+\gamma})/kT} - F_{\delta+\gamma} \bar{n}_{\delta+\gamma}(t) \right\} \\ & + \sum_{\delta=1}^{\delta+\gamma-1} A_{\delta,\delta+\gamma} \left\{ \bar{n}_{\delta}(t) \bar{n}_{\delta+\gamma}(t) - F_{\delta}(t) e^{-(F_{\delta+\gamma} + F_{\delta} - F_{\delta+\gamma})/kT} \right\}. \quad (4-58) \end{aligned}$$

The transition rates $A_{\delta,\gamma}$ are not written explicitly as a function of time although some changes in time are implied by the term $\bar{n}_{\delta+\gamma}(t) + 1$. For most applications, the number of available energy levels is large enough to allow $\bar{n}_{\delta+\gamma}(t) \ll 1$. This topic will receive further discussion in succeeding chapters.

The form of Eq. (4-58) implies that $A_{\delta,\gamma}$ is an average probability per unit time per cluster of γ molecules per cluster of δ molecules that clusters of δ molecules will join with clusters of γ molecules to form a cluster of $\delta+\gamma$ molecules. It is apparent that

$$A_{\delta,\gamma} e^{-(F_{\delta} + F_{\gamma} - F_{\delta+\gamma})/kT} \equiv B_{\delta+\gamma,\gamma} \quad (4-59)$$

is the probability per unit time per cluster of $\delta+\gamma$ molecules that a cluster of $\delta+\gamma$ molecules will separate into a cluster of δ molecules and a cluster of γ molecules. The evaporation rate $B_{\delta+\gamma,\gamma}$ is the growth rate multiplied by a free-energy barrier term. The free-energy barrier occurs because the molecules bound in a cluster must escape a potential

well to evaporate. Because a distribution of energy levels is imposed by the scattering steady-state condition, there will always be a probability that some molecules will escape. The evaporation rate can be written in another useful form by combining Eq. (4-59) and (4-57), and then using the delta function and Eq. (4-55) for the density of states. The result is

$$B_{\alpha+\delta,\delta} = 2\pi \sum_{ijk} \delta(\omega_{i(\alpha+\delta)} - \omega_{jk\delta}) \\ \times \omega_{i(\alpha+\delta)jk\delta}^2 \left(\bar{n}_{k\delta}(t) + 1 \right) \rho_{i(\alpha+\delta)} \quad (4-60)$$

in terms of average growth and evaporation probabilities, the master equation, Eq. (4-58) becomes

$$\frac{\partial P_{\delta}(t)}{\partial t} = \sum_{\gamma=1}^{\infty} \left\{ B_{\delta+\gamma,\gamma} P_{\delta+\gamma}(t) - A_{\delta,\gamma} \tilde{n}_{\gamma}(t) P_{\delta}(t) \right\} \\ + \sum_{\gamma=1}^{\delta-1} \left\{ A_{\delta-\gamma,\gamma} \tilde{n}_{\gamma}(t) P_{\delta-\gamma}(t) - B_{\delta,\gamma} P_{\delta}(t) \right\} \quad (4-61)$$

Another useful form of the master equation is found by transforming Eq. (4-61) into the form of the Pauli master equation. This can be accomplished by taking $\gamma = \alpha - \delta$ in the first term and $\gamma = \delta - \alpha$ in the second. After defining a transition rate as

$$W_{\delta\alpha}(t) = B_{\alpha,\alpha-\delta} h(\alpha-\delta) + A_{\alpha,\delta-\alpha} \tilde{n}_{\delta-\alpha}(t) h(\delta-\alpha) \quad , \quad (4-62)$$

where

$$h_{ij}(t) = \begin{pmatrix} 1, & i = j \\ 0, & i \neq j \end{pmatrix}$$

the Heaviside step function, we obtain

$$\frac{\partial P_i(t)}{\partial t} = \sum_{j=1}^{\infty} \{W_{ji}(t) P_j(t) - W_{ij}(t) P_i(t)\} \quad (4-63)$$

Summing this equation over i proves that probability is conserved. The Pauli master equation can also be written in matrix form; i.e., if we define a vector

$$\vec{P}(t) \equiv P_i(t) \quad , \quad (4-64)$$

and a matrix

$$\underline{L}(t) \equiv L_{\alpha\alpha}(t) = W_{\beta\alpha}(t) - \delta_{\alpha\alpha} \sum_{\beta} W_{\beta\alpha}(t) \quad , \quad (4-65)$$

then Eq. (4-63) can be written as

$$\frac{\partial \vec{P}(t)}{\partial t} = \underline{L}(t) \vec{P}(t) \quad . \quad (4-66)$$

The previous equation is nonlinear because the elements of the matrix operator $\underline{L}(t)$ depend on $\vec{P}(t)$. It can be proven that the determinant of $\underline{L}(t)$ is zero by noting that $W_{\alpha\alpha}(t) = 0$ and using Eq. (4-65) to show

that the diagonal term in any column is the sum of all the other terms in that column.

This concludes what we believe is the first derivation of the master equation for homogeneous nucleation from quantum mechanics. This equation reduces to the same form as the master equation assumed by Zel'dovich (1942), it is completely self-consistent, and the cluster distribution function for a system in energy equilibrium only is a natural result. It is not necessary to introduce what may be an ambiguous equilibrium distribution from statistical mechanics to find a relationship between $A_{\delta,\gamma}$ and $B_{\delta+\gamma,\gamma}$. We will investigate some formal solutions of the master equation in Chapter 5.

CHAPTER 5

SOLUTIONS OF THE MASTER EQUATION

The general master equation for nucleation was developed in Ch. 4. We now shall solve various forms of the master equation and analyze the applicability of these solutions to nucleation experiments. First, we will solve the vector form, Eq. (4-66), in the special case where the operator, $\underline{L}(t)$, is constant in time. This result (which is valid over short periods of time) is an eigenvalue solution and indicates that the system decays exponentially toward an infinite-time distribution. The operator equations for the first eigenvector (eigenvalue = 0) give no apparent information about the infinite-time probability distribution because they consist of many independent equations. We develop two infinite-time solutions: (1) the equilibrium solution, found by setting the time rate of change of the probability for every cluster to zero, and (2) the steady-state solution, characterized by the same probability current at every cluster size. The equilibrium solution is the equilibrium distribution of cluster probabilities in terms of the monomer chemical potential and eigenenergies of clusters. In terms of cluster free energies our distribution is the same as Wergeland's, described by ter Haar (1954, p. 217).

We prove that the most important terms in the master equation are the ones representing monomer accretion and evaporation. Elimination of all terms, except those for monomer accretion and evaporation, from the general master equation yields the monomer-controlled master equation. We solve the monomer-controlled master equation for the steady-state probability distribution and current. Our expression for the current

is similar to results of earlier derivations; however, the steady-state probability distribution (obtained simultaneously in our derivation) has not been reported elsewhere. See, for example, McDonald (1963) and Abraham (1974, p. 84). The steady-state distribution is eliminated by somewhat dubious means in McDonald's derivation of the steady-state current. Our equation for the steady-state current contains a summation. For many physical situations the sum can be converted to an integral that can be approximated by the method of steepest descent. The method of steepest descent defines a critical cluster as one whose rate of monomer accretion equals its rate of monomer evaporation. The steady-state solution provides a rate equation for a complete description of the cluster distribution (including monomers) if the time constant for monomer depletion is long compared to a time constant for establishment of a steady-state current.

We define a time constant for monomer depletion and determine the time constant for establishment of a steady-state current by converting the monomer-controlled master equation to a linear (constant monomer supply) Fokker-Plank equation that can be solved for the lowest eigenvalues (inverse time constants). To solve it, we transform the Fokker-Plank equation to an equivalent Schrödinger master equation and thereby obtain a potential function that describes the behavior of the distribution function. We find that the potential function has a minimum at the critical cluster size. Formal solution of the Schrödinger master equation (by separation of variables) yields an infinite-time term plus a time-dependent part that is a function of eigenvectors and eigenvalues. The time constant for formation of a steady-state distribution (the infinite time solution) is the inverse of the smallest nonzero eigenvalue.

The potential is symmetric about the minimum value at the critical cluster size; hence, we can obtain the smallest eigenvalues by the harmonic oscillator approximation. The largest time constant (smallest nonzero eigenvalue) has the same form as an expression by Abraham (1974, p. 101) for the characteristic time required to establish a steady-state distribution. Our result is twice as high as Abraham's. Application of this factor of two to Abraham's result yields close agreement with some values obtained by numerical experiments [Abraham (1974, Table 5-6)]. Typical numerical values indicate that the steady-state distribution is usually established on a time scale that is short compared to the time scale for monomer depletion.

The time-dependent behavior of the cluster distribution is described by solutions of the vector form of the Pauli master equation, Eq. (4-66). Unfortunately, the Pauli master equation represents an infinite number of nonlinear partial differential equations, for which no known analytic solutions exist. The nonlinearity occurs because the matrix operator, $\underline{L}(t)$, is a function of the number (probability) distribution. This functional dependence can be displayed in matrix form by noting that $\underline{L}(t)$ is a function of the matrix $\underline{W}(t)$ only [see Eq. (4-65)]. The elements of $\underline{W}(t)$ are given by Eq. (4-62). The matrix $\underline{W}(t)$ can be written as a function of three triangular matrices:

$$\underline{W}(t) = \tilde{n}(t) \underline{A} + \underline{B}, \quad (5-1)$$

where

$$\underline{\tilde{n}}(t) = \begin{pmatrix} 0 & \tilde{n}_1(t) & \tilde{n}_2(t) & \tilde{n}_3(t) & \dots \\ 0 & 0 & \tilde{n}_1(t) & \tilde{n}_2(t) & \dots \\ 0 & 0 & 0 & \tilde{n}_1(t) & \dots \\ \vdots & \vdots & \vdots & \vdots & \end{pmatrix}, \quad (5-2)$$

$$\underline{A} = \begin{pmatrix} 0 & 0 & 0 & \dots \\ A_{21} & 0 & 0 & \dots \\ A_{32} & A_{31} & 0 & \dots \\ A_{43} & A_{42} & A_{41} & \dots \\ \vdots & \vdots & \vdots & \end{pmatrix}, \quad (5-3)$$

and

$$\underline{B} = \begin{pmatrix} 0 & B_{21} & B_{32} & B_{43} & \dots \\ 0 & 0 & B_{31} & B_{42} & \dots \\ 0 & 0 & 0 & B_{41} & \dots \\ \vdots & \vdots & \vdots & \vdots & \end{pmatrix}. \quad (5-4)$$

The matrices demonstrate that terms representing monomer accretion and evaporation lie closest to the diagonal, terms representing dimer accretion and evaporation are next, etc. The most important processes are monomer accretion and evaporation (we will discuss this point later); hence, $\underline{W}(t)$ is approximately a tridiagonal matrix with zeros for diagonal elements. Over periods of time that are short compared to the characteristic time for monomer change, we can regard the matrices $\underline{\tilde{n}}(t)$ and $\underline{L}(t)$ as constant and hence can treat Eq. (4-66) as a linear equation to study the properties of cluster evolution. For this purpose we write Eq. (4-66) as

$$\frac{\partial \vec{P}(t)}{\partial t} \equiv \underline{L}(t_0) \vec{P}(t) \equiv \underline{L} \vec{P}(t) \quad , \quad (5-5)$$

where the argument t_0 indicates a particular probability distribution (calculated at $t = t_0$) for computing the constant matrix operator $\underline{L}$.

A formal solution of Eq. (5-5) can be found by methods from Oppenheim, Shuler, and Weiss (1971). By separating the time and cluster-size variables, we obtain the following solution:

$$\vec{P}(t) \approx \sum_I C_I \vec{\psi}_I e^{-\Lambda_I (t - t_0)} \quad , \quad (5-6)$$

where the eigenvalues, Λ_I , and eigenvectors, $\vec{\psi}_I$ can be obtained from the eigenvalue equation,

$$\underline{L} \vec{\psi}_I = -\Lambda_I \vec{\psi}_I \quad . \quad (5-7)$$

The C_I denotes expansion coefficients that allow us to write the solution as a function of all possible eigenvalues and eigenvectors. The subscript I identifies each eigenvalue and eigenvector. In addition to the eigenvalue equation, Eq. (5-7), there is the adjoint equation,

$$\underline{L}^\dagger \vec{\phi}_J = -\Lambda_J^* \vec{\phi}_J \quad . \quad (5-8)$$

The eigenvectors $\vec{\psi}_I$ and $\vec{\phi}_J$ are in dual spaces. We can prove that if the eigenvalues are not degenerate the dual vectors are orthogonal. If we multiply Eq. (5-7) by $\vec{\phi}_J^\dagger$, multiply Eq. (5-8) by $\vec{\psi}_J^\dagger$, take the adjoint of the last result, and subtract the two equations we obtain

$$(\Lambda_I - \Lambda_J) \vec{\phi}_J^\dagger \vec{\psi}_I = 0 \quad , \quad (5-9)$$

where $\vec{\phi}_J^\dagger \vec{\psi}_I$ is the scalar product. The orthogonality condition,

$$\vec{\phi}_J^\dagger \vec{\psi}_I = \delta_{IJ} \quad , \quad (5-10)$$

is implied by Eq. (5-9). The orthogonality condition can be used to find the expansion coefficients. We multiply Eq. (5-6) (with $t = t_0$) by $\vec{\phi}_J^\dagger$ and do the summation with the aid of the delta function to obtain

$$C_I = \frac{\vec{\phi}_I^\dagger \vec{p}(t_0)}{\vec{\phi}_I^\dagger \vec{\psi}_I} \quad . \quad (5-11)$$

Physical considerations imply that the eigenvalues must all have a real, positive part and that the lowest eigenvalue must be zero. The latter

part of this statement can be proven by noting that Eq. (4-65) implies

$$\sum_{\alpha} L_{\alpha\beta} = 0 \quad . \quad (5-12)$$

If we define a row vector as

$$\vec{\Phi}_0^{\dagger} = (1, 1, 1, \dots) \quad , \quad (5-13)$$

Eq. (5-12) is equivalent to

$$\vec{\Phi}_0^{\dagger} \underline{L} = 0 \quad . \quad (5-14)$$

The adjoint of Eq. (5-14) is

$$\underline{L}^{\dagger} \vec{\Phi}_0 = 0 \quad ; \quad (5-15)$$

hence, comparison of Eqs. (5-8) and (5-15) implies

$$\Lambda_0^* = 0 \quad . \quad (5-16)$$

From Eq. (5-16) we find $\Lambda_0 = 0$; hence, we obtain from Eq. (5-7):

$$\underline{L} \vec{\Psi}_0 = 0 \quad . \quad (5-17)$$

The time rate of change of probability must be zero at $t = \infty$; hence, from Eq. (5-5):

$$\underline{L} \vec{P}(\infty) = 0 \quad . \quad (5-18)$$

We infer from Eqs. (5-17) and (5-18) that there is an infinite-time solution for $\underline{L}$ calculated by any probability distribution [see Eqs. (4-65) and (5-1)] and that

$$\vec{\Psi}_0 = \vec{P}(\infty) \quad . \quad (5-19)$$

From Eq. (5-11) for C_I and Eq. (5-19) for $\vec{\Psi}_0$ we find that the first expansion coefficient is

$$C_0 = \frac{\vec{\Phi}_0^+ \vec{P}(t_0)}{\vec{\Phi}_0^+ \vec{P}(\infty)} = 1 \quad . \quad (5-20)$$

The second equality in Eq. (5-20) follows from conservation of probability. The short-time solution of the master equation is a result of combining Eq. (5-6) for $\vec{P}(t)$, Eq. (5-11) for C_I , Eq. (5-20) for C_0 , and Eq. (5-19) for $\vec{\Psi}_0$:

$$\vec{P}(t) = \vec{P}(\infty) + \sum_{I=1}^{\infty} \frac{\vec{\Phi}_0^+ \vec{P}(t_0)}{\vec{\Phi}_0^+ \vec{\Psi}_I} \vec{\Psi}_I e^{-\Lambda_I (t - t_0)} \quad . \quad (5-21)$$

Although the time dependence of eigenvectors and eigenvalues is not explicitly shown, it is implied that the eigenvectors, $\vec{\Psi}_I$, and the eigenvalues, Λ_I , are to be computed from Eq. (5-7) by using the value of $\underline{L}$ at $t = t_0$. The dual eigenvectors, $\vec{\Phi}_J$, can be computed from Eq. (5-8).

Equation (5-21) shows how $\vec{P}(t)$ approaches the infinite-time solution; however, it provides no new information about what this solution

is. This information should come from Eq. (5-18), which has a solution only when the determinant of $\underline{L}$ is zero. Setting the determinant of $\underline{L}$ to zero should provide information about the probability distribution because $\underline{L}$ is a function of that quantity. However, we have proven in Ch. 4 that the determinant of $\underline{L}$ is zero for any probability distribution. The determinant is zero because Eq. (5-18) represents a set of many independent equations. This is evident if we return to the form of the master equation given by Eq. (4-61). If we define a probability current as

$$I_{\alpha,\beta}(t) = A_{\alpha,\beta} \left\{ P_{\alpha}(t) \tilde{n}_{\beta}(t) - P_{\alpha+\beta}(t) e^{-(F_{\alpha} + F_{\beta} - F_{\alpha+\beta})/kT} \right\}, \quad (5-22)$$

the master equation can be written as

$$-\frac{\partial P_{\alpha}(t)}{\partial t} = \sum_{\beta=1}^{\alpha-1} I_{\alpha-\beta,\beta}(t) - \sum_{\beta=1}^{\infty} I_{\alpha,\beta}(t). \quad (5-23)$$

When the system is locally in complete equilibrium at $t = t_{\infty}$,

$$\left. \frac{\partial P_{\alpha}(t)}{\partial t} \right|_{t=\infty} = 0, \quad (5-24)$$

for every α , and

$$\sum_{\beta=1}^{\alpha-1} I_{\alpha-\beta,\beta}^{(eq)} - \sum_{\beta=1}^{\infty} I_{\alpha,\beta}^{(eq)} = 0. \quad (5-25)$$

Application of Eq. (5-25) to monomers ($\alpha = 1$) yields

$$\sum_{\beta=1}^{\infty} I_{1,\beta}(\text{eq}) = 0 \quad . \quad (5-26)$$

All rate coefficients, $A_{1,\beta}$, in Eq. (5-22) are linearly independent; hence, the only solution for Eq. (5-26) is the trivial one: the coefficient of each $A_{1,\beta}$ is equal to zero. The solution implies

$$I_{1,\beta}(\text{eq}) = 0 \quad . \quad (5-27)$$

Application of Eq. (5-25) to the dimer ($\alpha = 2$) and use of Eq. (5-27) yields

$$\sum_{\beta=1}^{\infty} I_{2,\beta}(\text{eq}) = 0 \quad . \quad (5-28)$$

All rate coefficients, $A_{2,\beta}$, in Eq. (5-22) are linearly independent; hence, the coefficients of each $A_{2,\beta}$ is also zero. Repeated application of the procedure for $\alpha = 3, 4, \dots$ proves that the coefficient of every $A_{\alpha,\beta}$ in Eq. (5-22) is zero. Setting these coefficients to zero yields:

$$\frac{P_{\alpha+\beta}(\text{eq})}{P_{\alpha}(\text{eq}) \tilde{n}_{\beta}(\text{eq})} = e^{-(F_{\alpha+\beta} - F_{\alpha} - F_{\beta})/kT} \quad . \quad (5-29)$$

By combining Eq. (5-29) with results from Ch. 4, we can find the equilibrium number distribution in terms of the chemical potential. After

using Eq. (4-30) [summed over $i(\alpha)$] and Eq. (4-50) (at $t = \infty$) to calculate the quantity on the left of Eq. (5-29) we obtain

$$\frac{P_{\alpha+\beta}(\text{eq})}{P_{\alpha}(\text{eq}) n_{\beta}(\text{eq})} = e^{-(F_{\alpha+\beta} - F_{\alpha} - F_{\beta})/kT}$$

$$e^{\left[G_{\alpha+\beta}(\text{eq}) - G_{\alpha}(\text{eq}) - G_{\beta}(\text{eq}) \right]/kT} \quad (5-30)$$

From Eqs. (5-29) and (5-30) we find that a condition for equilibrium is

$$G_{\alpha+\beta}(\text{eq}) = G_{\alpha}(\text{eq}) + G_{\beta}(\text{eq}) \quad (5-31)$$

Repeated application of Eq. (5-31) with $\alpha = \beta = 1$; $\alpha = 2, \beta = 1$; etc, produces the result

$$G_{\alpha}(\text{eq}) = \alpha G_1(\text{eq}) \equiv \alpha \mu \quad (5-32)$$

where μ is the chemical potential of a monomer when the system is in equilibrium. The chemical potential, μ , is the energy required to remove a molecule from the system; hence, the physical interpretation of Eq. (5-32) is: all clusters are free to exchange molecules when the system is in complete equilibrium. The form of the Gibbs free energy given by Eq. (5-32) is introduced ad hoc (from the physical interpretation) by ter Haar (1954, p. 217) in his discussion of Wergeland's theory of condensation. Substitution of Eq. (5-32) into Eq. (4-50) implies that the equilibrium probability distribution is proportional to

$$\tilde{n}_{\alpha}(\text{eq}) = e^{-(F_{\alpha} - \alpha \mu)/kT} \quad (5-33)$$

Next, substitution of Eq. (5-33) into Eq. (4-52) implies that the equilibrium probability distribution of energy levels is proportional to

$$\tilde{n}_{i\alpha}(\text{eq}) = e^{-(\epsilon_{i\alpha} - \mu \alpha)/kT} \quad (5-34)$$

Finally, substitution of Eq. (5-34) into Eq. (4-45) yields the number distribution of energy levels

$$\bar{n}_{i\alpha}(\text{eq}) = \frac{e^{-(\epsilon_{i\alpha} - \mu \alpha)/kT}}{1 - e^{-(\epsilon_{i\alpha} - \mu \alpha)/kT}} \quad (5-35)$$

The preceding equation will be used extensively in equation-of-state and saturation-line analysis in Ch. 6.

There is another infinite-time solution known as the steady-state solution. This solution is attainable if we make a physical assumption that can be justified by analysis of the equilibrium distribution and transition rates. The assumption is: clusters change size by absorption and evaporation of monomers. We note that the growth term for clusters of α molecules in the current defined by Eq. (5-22) is

$$A_{\alpha,\beta} P_{\alpha}(t) \tilde{n}_{\beta}(t) \quad .$$

The kinetic coefficient, $A_{\alpha,\beta}$, can be related to the cross section; hence, we assume that it is a function that varies slowly with β . The growth is controlled to a large extent by $\tilde{n}_{\beta}(t)$; hence, if $\tilde{n}_1(t)$ is

much larger than any other $\tilde{n}_\beta(t)$, the growth will be controlled by monomers. The relatively large number of monomers is illustrated by using Eqs. (5-33) and (4-30) to find the ratio of probabilities

$$\frac{P_{\alpha+1}(\text{eq})}{P_\alpha(\text{eq})} = e^{-(F_{\alpha+1} - F_\alpha - \mu)/kT} \quad (5-36)$$

We will prove in Ch. 6 that $F_{\alpha+1} - F_\alpha \gg \mu$ for small clusters, that $\mu < 0$, and that $F_{\alpha+1} - F_\alpha < 0$; hence, Eq. (5-36) implies that the smallest cluster (the monomer) has the highest probability of existence and that it is much higher than the dimer probability. If the preceding statement is true in the equilibrium state it will also be true in the supersaturated state characterized by excess monomers. The evaporation process for clusters of α molecules is described by the second term of the equation for the current, Eq. (5-22). The dominant factor in this term is the free-energy barrier term

$$e^{-(F_\alpha + F_\beta - F_{\alpha+\beta})/kT}$$

If we define a free energy per molecule in a cluster of α molecules as

$$f_\alpha = \frac{F_\alpha}{\alpha} \quad , \quad (5-37)$$

the evaporation rate is proportional to

$$e^{-\alpha (f_\alpha - f_{\alpha+\beta})/kT} e^{-\beta (f_\beta - f_{\alpha+\beta})/kT}$$

For evaporation from clusters of α molecules the free-energy barrier is a minimum when β is unity, because β is the dominant factor in $\beta (f_\beta - f_{\beta+\alpha})$.

For our studies of monomer-controlled nucleation we will define

$$A_\alpha \equiv A_{\alpha,1} \quad , \quad (5-38)$$

and

$$I_{\alpha,1} \equiv I_\alpha \quad . \quad (5-39)$$

From Eqs. (5-22, with $\beta = 1$), (5-38), and (5-37) we find that the monomer-controlled current is

$$I_\alpha(t) = A_\alpha \left\{ P_\alpha(t) \tilde{n}_1(t) - P_{\alpha+1}(t) e^{-(F_\alpha + F_1 - F_{\alpha+1})/kT} \right\} . \quad (5-40)$$

The monomer controlled master equation obtained from Eq. (5-23) is

$$\frac{\partial P_\alpha(t)}{\partial t} = I_{\alpha-1}(t) - I_\alpha(t) \quad . \quad (5-41)$$

If we define a constant probability current as

$$I = I_\alpha(ss) = I_{\alpha-1}(ss) \quad (5-42)$$

and substitute Eq. (5-42) into the master equation, Eq. (5-41), it is evident that we obtain another infinite-time solution as defined by

Eq. (5-24). We use the notation $I_{\alpha}(t = \infty) = I_{\alpha}(ss)$ to distinguish the infinite-time steady-state solution from the infinite-time equilibrium solution defined by Eq. (5-25). The steady-state solution requires a constant supply of monomers, $I_0 = I$, flowing into the local region from an external source. If there is such a constant monomer supply there is no limit to the maximum cluster size; however, in most physical situations the very large clusters are removed from the local volume. For each monomer that flows through the steady-state probability distribution there is a very large cluster produced; i.e., $I_{\alpha^*} = 0$ and

$$\frac{\partial P_{\alpha^*}(t)}{\partial t} = I_{\alpha^*-1} = I, \quad (5-43)$$

where α^* is some large cluster size. Physical applications are diffusion cloud chamber experiments and atmospheric studies. In these systems rising gas that has been heated provides a monomer source and large clusters are removed by the forces of gravity.

The steady-state distribution of cluster sizes is defined by taking $I_{\alpha} = I$ in Eq. (5-40). For convenience of notation in evaluating the steady-state distribution we introduce the monomer evaporation rate B_{α} . From Eqs. (4-59) for $B_{\alpha,1}$ and (5-38) for $A_{\alpha,1}$:

$$B_{\alpha} \equiv B_{\alpha,1} = A_{\alpha-1} e^{-(F_{\alpha-1} - F_{\alpha} + F_1)/kT}. \quad (5-44)$$

Also, the number of monomers as a function of the monomer Gibbs free energy is, from Eq. (4-50),

$$\tilde{n}_1(ss) = e^{-\left[F_1 - G_1(ss)\right]/kT} \quad (5-45)$$

To obtain a recursion formula for the steady-state probability distribution, we combine Eqs. (5-40) and (5-42) for I; Eq. (5-44) for B_α ; Eq. (5-45) for $\tilde{n}_1(ss)$; and then rearrange terms. The result is

$$P_\alpha(ss) = P_{\alpha-1}(ss) e^{-\left[F_{\alpha-1} - F_\alpha + G_1(ss)\right]/kT} - I B_\alpha^{-1} \quad (5-46)$$

We find that by successive substitution, Eq. (5-46) can be solved for the steady-state distribution function:

$$P_\alpha(ss) = P_1(ss) \frac{e^{-\left[F_\alpha - \alpha G_1(ss)\right]/kT}}{e^{-\left[F_1 - G_1(ss)\right]/kT}}$$

$$\left\{ 1 - I \sum_{\beta=2}^{\alpha} \frac{e^{-\left[F_1 - G_1(ss)\right]/kT}}{B_\beta P_1(ss) e^{-\left[F_\beta - \beta G_1(ss)\right]/kT}} \right\} \quad (5-47)$$

The physical interpretation of Eq. (5-47) becomes more apparent if we define a saturation ratio as

$$S \equiv \frac{P_1(ss)}{P_1(eq)} \quad (5-48)$$

The saturation ratio is a measure of the excess number of monomers. We can write the monomer Gibbs free energy as a function of the chemical potential and saturation ratio by combining Eq. (5-45) for $\tilde{n}_1(ss)$, Eq. (5-33) for $\tilde{n}_1(eq)$, Eq. (4-30) to relate probability and number, and Eq. (5-48) for S;

$$G_1(ss) = \mu + kT \ln S \quad . \quad (5-49)$$

The steady-state probability distribution, Eq. (5-47) can be written in simpler form by substituting Eq. (5-49) into Eq. (5-47) and then using Eq. (5-33) for $\tilde{n}_\alpha(eq)$ and Eq. (4-30) to relate probability and number to obtain

$$P_\alpha(ss) = S^\alpha P_\alpha(eq) \left\{ 1 - I \sum_{\beta=2}^{\alpha} \frac{1}{B_\beta S^\beta P_\beta(eq)} \right\} \quad . \quad (5-50)$$

The steady-state current, I , can be obtained by imposing a boundary condition on Eq. (5-50). To ensure that $P_\alpha(ss)$ does not become infinite (because of the S^α factor), we require that the factor in braces, $\{\}$, asymptotically approach zero as α approaches infinity. This enables us to obtain an expression for the probability current,

$$I = \sum_{\beta=2}^{\infty} \left\{ \frac{1}{B_\beta S^\beta P_\beta(eq)} \right\}^{-1} \quad . \quad (5-51)$$

The series summation converges by the ratio test. Convergence by the ratio test requires that

$$\lim_{\beta \rightarrow \infty} \frac{B_\beta S^\beta P_\beta(eq)}{B_{\beta+1} S^{\beta+1} P_{\beta+1}(eq)} < 1 \quad . \quad (5-52)$$

For large β , $B_\beta \approx B_{\beta+1}$ and $P_\beta(eq) \approx P_{\beta+1}(eq)$; hence, the series converges, by the ratio test, for $S > 1$. Substitution of Eq. (5-51) into Eq. (5-50) yields the steady-state probability distribution as a function of the equilibrium probability distribution $P_\alpha(eq)$, the saturation ratio S , and the monomer evaporation rate B_α :

$$P_{\alpha}(ss) = S^{\alpha} P_{\alpha}(eq) \left\{ 1 - \frac{\sum_{\beta=2}^{\alpha} [B_{\beta} S^{\beta} P_{\beta}(eq)]^{-1}}{\sum_{\beta=2}^{\alpha} [B_{\beta} S^{\beta} P_{\beta}(eq)]^{-1}} \right\} . \quad (5-53)$$

A current equivalent to that from Eq. (5-51) has been derived by Courtney (1962). He used the law of mass action from chemical kinetics and a constant-current equation equivalent to Eq. (5-42). Diffusion cloud chamber experiments measure the specific rate of droplet production from a thin region of the experimental device; hence, a number distribution obtained from the probability distribution is the physically observed quantity. This number distribution is obtained by defining the constant implied by Eq. (4-30). Let

$$N \equiv \sum_{\alpha} \tilde{n}_{\alpha} , \quad (5-54)$$

then

$$\tilde{n}_{\alpha} = N P_{\alpha} . \quad (5-55)$$

The current, I , is a probability current; hence, Eq. (5-55) suggests that we define a steady-state rate-of-droplet production per unit volume as

$$J \equiv \frac{N}{V} I . \quad (5-56)$$

We shall refer to J as the number current.

To express J in terms of steady-state number densities, we combine the preceding equation with Eq. (5-42) for I , Eq. (5-40) for $I_{\alpha}(ss)$, Eq. (5-44) for B_{β} , and Eq. (5-55) for N to obtain

$$J = A_{\alpha} \tilde{n}_1(ss) \frac{\tilde{n}_{\alpha}(ss)}{V} - B_{\alpha+1} \frac{\tilde{n}_{\alpha+1}(ss)}{V} . \quad (5-57)$$

Also, the number current can be obtained by combining Eq. (5-56) for the definition of J , Eq. (5-51) for the probability current, Eq. (5-55) for F_α , and Eq. (5-33) for the equilibrium number distribution $\tilde{n}_\alpha$:

$$J = \frac{1}{V} \left\{ \sum_{\beta=2}^{\infty} \frac{e^{(F_\beta - \beta \mu)/kT}}{B_\beta S^\beta} \right\}^{-1} \quad (5-58)$$

If methods for calculating F_β , μ , and B_β are given (to be developed in Chs. 6, 7, and 8), Eq. (5-58) is in the proper form for calculating the droplet-formation rate measured in diffusion-cloud-chamber experiments.

If S is not too large, most of the contributions to the sum in Eq. (5-58) will come from terms where β is large. If β is large F_β and B_β are continuous; hence, we can replace the sum by an integral. Before doing this, we define a free-energy difference as

$$\Omega_\beta = F_\beta - \beta (\mu + kT \ln S) - kT \ln B_\beta ; \quad (5-59)$$

then Eq. (5-58) for the number current becomes

$$J \approx \frac{1}{V} \left\{ \int_{\beta=2}^{\infty} d\beta e^{\Omega_\beta/kT} \right\}^{-1} \quad (5-60)$$

The exponent Ω_β in Eq. (5-60) has a maximum value; hence, the integral can be approximated by the method of steepest descent [Spiegel (1964, p. 274)]. By this method Eq. (5-60) becomes

$$J \approx \frac{B_\Gamma}{V} \left[- \frac{1}{2\pi kT} \Omega_\beta \right]_{\beta=\Gamma}^{1/2} e^{-[F_\Gamma - \Gamma (\mu + kT \ln S)]/kT} \quad (5-61)$$

where the prime implies differentiation with respect to cluster size and Γ is the value of α where n_2 is at its maximum. The critical cluster size Γ is determined from

$$\left(\hat{F}'_{\alpha} - kT \frac{\hat{B}'_{\alpha}}{\hat{B}_{\alpha}} \right) \bigg|_{\alpha=\Gamma} = \mu + kT \ln S = G_1(ss) . \quad (5-62)$$

We can use the relation between growth and evaporation coefficients, Eq (5-44), to write the preceding results in more useful form. From Eq. (5-44) we find that

$$F_{\alpha+1} - F_{\alpha} = kT \ln \left(\frac{B_{\alpha+1}}{B_{\alpha}} \right) = F_1 + kT \ln \left(\frac{B_{\alpha}}{A_{\alpha}} \right) . \quad (5-63)$$

We calculate the derivative of F_{α} with respect to α by

$$\hat{F}'_{\alpha} = F_{\alpha+1} - F_{\alpha} , \quad (5-64)$$

and use a similar procedure for $\hat{B}'_{\alpha}$. If we assume B_{α} is a slowly varying function of α ,

$$\ln \left(\frac{B_{\alpha+1}}{B_{\alpha}} \right) \approx \ln \left(1 + \frac{\hat{B}_{\alpha}}{B_{\alpha}} \right) \approx \frac{\hat{B}_{\alpha}}{B_{\alpha}} . \quad (5-65)$$

Substitution of Eqs. (5-64) and (5-65) into Eq. (5-63) yields

$$\hat{F}'_{\alpha} - kT \frac{\hat{B}_{\alpha}}{B_{\alpha}} = F_1 + kT \ln \left(\frac{B_{\alpha}}{A_{\alpha}} \right) . \quad (5-66)$$

By substituting Eq. (5-66) into Eq. (5-62) and employing Eq. (5-45) for $G_1(ss)$, we find the following equation [equivalent to Eq. (5-62)] for determining the critical cluster size, Γ ,

$$\tilde{n}_1(ss) A_{\Gamma} = B_{\Gamma} . \quad (5-67)$$

The second derivative of the free-energy difference Ω_{α}'' required in Eq. (5-61), can be written in terms of first derivatives of kinetic coefficients. From Eqs. (5-59) for Ω_{β} and (5-63) we derive

$$\Omega_{\alpha}'' = \left(F_{\alpha}' - kT \frac{B_{\alpha}'}{B_{\alpha}} \right)' = kT \left(\ell_n \frac{B_{\alpha}'}{A_{\alpha}} \right)' . \quad (5-68)$$

The previous result and Eq. (5-55) for $\tilde{n}_{\alpha}(\text{eq})$ can be used to write the number current from Eq. (5-61) in a more compact form:

$$J = \left[\frac{1}{2\pi} \left(\ell_n \frac{A_{\alpha}'}{B_{\alpha}'} \right)' \Big|_{\alpha=\Gamma} \right]^{1/2} B_{\Gamma} S^{\Gamma} \frac{\tilde{n}_{\Gamma}(\text{eq})}{V} . \quad (5-69)$$

We find an equivalent equation by substituting Eq. (5-44) for B_{Γ} ; Eqs. (5-29) and (5-55) combined for $\tilde{n}_{\alpha}(\text{eq})$; and Eq. (5-48) for S into Eq. (5-69):

$$J = \left[\frac{1}{2\pi} \left(\ell_n \frac{A_{\alpha}'}{B_{\alpha}'} \right)' \Big|_{\alpha=\Gamma} \right]^{1/2} A_{\Gamma-1} \tilde{n}_1(ss) S^{\Gamma-1} \frac{\tilde{n}_{\Gamma-1}(\text{eq})}{V} . \quad (5-70)$$

From Eq. (5-53) it is evident that, approximately,

$$\tilde{n}_{\Gamma}(ss) \propto S^{\Gamma} \tilde{n}_{\Gamma}(\text{eq}) \quad ; \quad (5-71)$$

hence, Eqs. (5-69) and (5-70) have a physical interpretation. From Eq. (5-69) we see that the number current is the rate of evaporation of critical-size clusters modified by a coefficient to account for cluster growth. Similarly, Eq. (5-70) implies that the number current is the rate of growth of clusters containing one molecule less than the critical

size, modified by a coefficient to account for evaporation. The coefficient is the same for both interpretations because the rate of monomer growth is equal to the rate of evaporation for a critical-size cluster, see Eq. (5-67). The quantity

$$Z_{\Gamma} = \left[\frac{1}{2\pi} \left(\ln \frac{A_{\alpha}}{B_{\alpha}} \right) \right]_{\alpha=\Gamma}^{1/2} \quad (5-72)$$

is denoted as the Zel'dovich factor by many authors, see for example Abraham (1974, p. 87).

We have developed two methods for computing the number current, J . Both require equations for calculating F_{α} , μ , and B_{α} . The first method, Eq. (5-51), requires a summation over many terms and hence requires the use of a large computer. It has the advantage of no limitation on saturation ratio S ; i.e., at very large supersaturation the critical cluster size can become very small and therefore make the second method invalid. The second method, Eq. (5-69), has the advantage of simplicity of calculation and is expected to be nearly as accurate as the first method when the critical cluster size, Γ , is large (≥ 50). It will be very useful for comparisons with previous nucleation theories.

The equations for J were developed under the assumption that J is constant; i.e., monomers are continually added at a rate of J monomers/cm³ s. If the monomer supply is not replenished, $I_0 = 0$ in Eq. (5-41) and $I_{\alpha} = I$ (for $\alpha \geq 1$) can be considered to be slowly changing in time. Justification for this assumption will be developed later. Under these conditions Eqs. (5-41), (5-55), and (5-56) combine to yield a differential equation for the number of monomers:

$$\frac{d}{dt} \left(\frac{\tilde{n}_1(ss)}{V} \right) = -J \quad (5-73)$$

The previous equation suggests that a time constant for monomer depletion can be defined as

$$\tau \equiv \frac{1}{J} \frac{\tilde{n}_1(ss)}{V} \quad (5-74)$$

If τ is much longer than the characteristic time for formation of the distribution of clusters described by Eq. (5-53), Eqs. (5-73) and (5-58) for J [or (5-69) for J] form a valid set of equations for description of the cluster-distribution time evolution when the monomer supply is not constant. An important application of Eq. (5-73) is analysis of nucleation in nozzle expansions.

We have shown that the solution of the master equation in the form given by Eq. (5-5) is the sum of an infinite-time solution plus terms that exponentially decay (over a short period of time) toward zero [see Eq. (5-21)]. We have also found two infinite-time solutions for $P_\alpha(\infty)$: (1) the equilibrium solution $P_\alpha(eq)$ that is proportional to $\tilde{n}_\alpha(eq)$ given by Eq. (5-33) and (2) the steady-state solution $P_\alpha(ss)$ (valid for monomer accretion and evaporation) given by Eq. (5-53). An estimate of the smallest nonzero eigenvalue Λ_1 in Eq. (5-21) would provide information about the time scale for changes in the distribution function. Because the eigenvectors are infinite in length, it does not appear possible to find the smallest eigenvalue from Eq. (5-7). By converting the master equation into a continuum Fokker-Planck equation, we can obtain more insight into the time evolution of the probability

distribution. The simplest Fokker-Planck equation is obtained by Taylor series expansion of the monomer-controlled master equation. The latter equation can be obtained from Eq. (4-61) by taking only one term in the sum over γ :

$$\begin{aligned} \frac{\partial P_{\alpha}(t)}{\partial t} = & B_{\alpha+1} P_{\alpha+1}(t) - A_{\alpha} \tilde{n}_1(t) P_{\alpha}(t) \\ & - B_{\alpha} P_{\alpha}(t) + A_{\alpha-1} \tilde{n}_1(t) P_{\alpha-1}(t) . \end{aligned} \quad (5-75)$$

We shall define a drift vector as

$$X_{\alpha}(t) = \tilde{n}_1(t) A_{\alpha} - B_{\alpha} \quad (5-76)$$

and a diffusion coefficient as

$$Y_{\alpha}(t) = \tilde{n}_1(t) A_{\alpha} + B_{\alpha} . \quad (5-77)$$

Expansion of the monomer-controlled master equation, Eq. (5-75), by Taylor series and employment of the preceding equations for the drift vector and diffusion coefficient yield the Fokker-Planck equation,

$$\frac{\partial P_{\alpha}(t)}{\partial t} = \frac{1}{2} \frac{\partial^2}{\partial \alpha^2} \left[Y_{\alpha}(t) P_{\alpha}(t) \right] - \frac{\partial}{\partial \alpha} \left[X_{\alpha}(t) P_{\alpha}(t) \right] . \quad (5-78)$$

The preceding equation is nonlinear because the drift vector and diffusion coefficient are functions of $\tilde{n}_1(t)$. Our analysis will employ a technique similar to one used to analyze Eq. (4-66); i.e., we will assume

that the number density of monomers is either fixed or changes slowly enough to consider $\tilde{n}_1(t)$ constant over a short time, and look for solutions of Eq. (5-78) where Y_α and X_α are not functions of time. Effectively, we will be looking at steady-state solutions and at the rate at which the system approaches a steady state.

The Fokker-Planck equation, Eq. (5-78), can be derived from a second-order partial differential equation that has a unit diffusion coefficient by a method presented by Goel and Richter-Dyn (1974, p. 40). Given a Fokker-Planck equation of the type,

$$\frac{\partial \phi(z,t)}{\partial t} = \frac{1}{2} \frac{\partial^2 \phi(z,t)}{\partial z^2} - \frac{\partial}{\partial z} \left[Q(z) \phi(z,t) \right] , \quad (5-79)$$

it can be shown that this equation is equivalent to Eq. (5-78) (when X_α and Y_α are not functions of time) by the following transformation:

$$z(\alpha) = \int^\alpha d\beta Y_\beta^{-1/2} , \quad (5-80)$$

$$Q(z) = \left(X_\alpha - \frac{1}{4} Y_\alpha' \right) Y_\alpha^{-1/2} , \quad (5-81)$$

and

$$\Phi(z(\alpha), t) = Y_\alpha^{1/2} P_\alpha(t) . \quad (5-82)$$

The prime in Eq. (5-81) implies differentiation with respect to α . Because Eq. (5-78) can be derived from Eq. (5-79) by using the transformation equations, Eqs. (5-80) through (5-82), we will use Eq. (5-79) for our master equation.

A master equation in the form of Eq. (5-79) can be transformed into a Schrödinger master equation by

$$\phi(z,t) = v(z) u(z,t) \quad . \quad (5-83)$$

Substitution of Eq. (5-83) into Eq. (5-79) yields:

$$v(z) = \exp\left(\int^z dx Q(x)\right) \quad , \quad (5-84)$$

and

$$\frac{\partial u(z,t)}{\partial t} = \frac{1}{2} \frac{\partial^2 u(z,t)}{\partial z^2} - V(z) u(z,t) \quad , \quad (5-85)$$

where

$$V(z) \equiv \frac{1}{2} \left[\dot{Q}(z) + Q^2(z) \right] \quad . \quad (5-86)$$

The prime in Eq. (5-86) indicates differentiation with respect to z . It is evident that Eq. (5-85) has the form of the Schrödinger equation when $V(z)$ is considered a potential function. The potential can be written as a function of drift vectors and diffusion coefficients by substituting Eq. (5-81) for $Q(z)$ into Eq. (5-86) and using Eq. (5-80) for differential relations between z and α . We find that

$$V(\alpha) = \frac{Y_\alpha}{2} \left\{ \left(\frac{X_\alpha}{Y_\alpha} \right)^2 + \left(\frac{X_\alpha}{Y_\alpha} \right)' - \left[\left(\frac{1}{4} \ln Y_\alpha \right)' \right]^2 - \left(\frac{1}{4} \ln Y_\alpha \right) \right\} \quad . \quad (5-87)$$

The Schrödinger master equation, Eq. (5-85), is in a form that can be solved by many well-known techniques. For known values of $u(z,t)$, the probability distribution can be found by combining Eqs. (5-80) through (5-84) to obtain:

$$P_{\alpha}(t) = Y_{\alpha}^{-3/4} \exp\left(\int^{\alpha} d\beta \, X_{\beta}/Y_{\beta}\right) u(z(\alpha), t). \quad (5-88)$$

The potential function, Eq. (5-87), has many interesting features. The first term in the braces dominates except near a critical cluster size where the drift vector $X_{\alpha=\Gamma}$ is equal to zero. Let all terms of the potential, except the first term, be represented by

$$V_{\min}(\alpha) \equiv \frac{Y_{\alpha}}{2} \left(\frac{X_{\alpha}}{Y_{\alpha}}\right)' - \left\{ \left[\left(\frac{1}{4} \ln Y_{\alpha}\right)' \right]^2 + \left(\frac{1}{4} \ln Y_{\alpha}\right)'' \right\}, \quad (5-89)$$

then the potential can be written

$$V(\alpha) = \frac{1}{2} \frac{X_{\alpha}^2}{Y_{\alpha}} + V_{\min}(\alpha). \quad (5-90)$$

Note that the term in braces, $\{\}$, in Eq. (5-89) is negligible for reasonably smooth potential functions because it involves second derivatives and squares of first derivatives, while the first term is a function of the first derivative. From Eq. (5-90) it is evident that the potential function has a minimum value equal to $V_{\min}(\Gamma)$ at $\alpha = \Gamma$, the critical cluster size where the drift vector is zero, and that it has a parabolic shape near its minimum value. To find the critical cluster size Γ we set the drift vector of Eq. (5-76) to zero and determine that the implicit equation,

$$\tilde{n}_1(ss) A_\Gamma = B_\Gamma \quad , \quad (5-91)$$

must be solved for Γ . We have specified $\tilde{n}_1(t) = \tilde{n}_1(ss)$ as the steady-state value in Eq. (5-91) because Eqs. (5-79) through (5-90) are valid for a constant supply of monomers.

We note that Eq. (5-91) is identical to Eq. (5-67); hence, the critical cluster size determined by the location of the minimum value of the Schrödinger master-equation potential is the same as the critical cluster size determined by the location of the maximum value of the free-energy difference Ω_α . The critical-size cluster is one that has a growth rate by monomer addition equal to the monomer evaporation rate. The kinetic coefficients for growth are controlled by the number density of monomers; hence, the critical cluster size is determined by the saturation ratio [see Eqs. (5-91) and (5-48)]. The change in Helmholtz free energy for addition of a monomer to a critical-size cluster is approximately equal to the Gibbs free energy of a monomer [see Eq. (5-62)].

The time evolution of a set of clusters in the continuum approximation is given by solutions of the Schrödinger master equation, Eq. (5-85). We have solved Eq. (5-85) in Appendix III and the result is

$$u(z,t) = u(z,ss) + \sum_{I=1}^{\infty} \frac{(\psi_I, u(t_0))}{(\psi_I, \psi_I)} \psi_I(z) e^{-\Lambda_I (t - t_0)} \quad . \quad (5-92)$$

The scalar product $(\psi_I, u(t_0))$ is defined by Eq. (III-6) and Λ_I is an eigenvalue. The infinite-time solution is the steady-state

solution because the result is derived under the assumption of constant monomer density. The smallest nonzero value of Λ_I in the preceding equation, Λ_1 , is a measure of the rate at which some distorted distribution approaches the steady-state distribution (providing there is an external source of monomers to keep the number density of monomers constant). If the time constant for monomer depletion, τ , is much larger than Λ_1^{-1} , the system can be considered to evolve as a slowly varying steady-state distribution and Eq. (5-73) becomes a valid equation for determining the system evolution.

We can find an estimate of Λ_1 by expanding the drift vector X_α in a first-order Taylor series about the point $\alpha = \Gamma$ (where X_Γ is zero). This expansion leaves the eigenvalue equation, Eq. (III-4) [obtained from the Schrödinger master equation, Eq. (5-85)], in the form of a Schrödinger equation for a harmonic oscillator. From Eqs. (III-4) and (III-1) we obtain

$$\frac{d^2 \psi_I(z)}{dz^2} + 2 \left(\Lambda_I - V(z) \right) \psi_I(z) = 0 \quad . \quad (5-93)$$

The expansion for the drift vector is

$$X_{\alpha(z)} = a \left(z - z(\Gamma) \right) \quad , \quad (5-94)$$

where

$$a \equiv \left. \frac{dX_{\alpha(z)}}{dz} \right|_{z = z(\Gamma)} \quad . \quad (5-95)$$

We shall consider the origin of z space to be at $\alpha = \Gamma$, i.e., $z(\Gamma) = 0$. In the potential function, Eq. (5-90), we shall hold $V_{\min}(z(\alpha))$ constant at $V_{\min}(z(\Gamma)) = V_{\min}(\Gamma)$ and $Y_{\alpha(z)}$ constant at Y_{Γ} . If we let

$$E_I \equiv \Lambda_I - V_{\min}(\Gamma) , \quad (5-96)$$

the preceding equations, Eqs. (5-93) through (5-96), combine with Eq. (5-90) for $V(z(\alpha))$ to yield the Schrödinger wave equation for the harmonic oscillator,

$$\frac{d^2 \psi_I(z)}{dz^2} + 2 \left(E_I - \frac{1}{2} \frac{a^2}{Y_{\Gamma}} z^2 \right) \psi_I(z) = 0 . \quad (5-97)$$

The "eigenenergies" for the preceding equation are

$$E_I = \frac{a}{Y_{\Gamma}^{1/2}} \left\{ (I - 1) + \frac{1}{2} \right\} . \quad (5-98)$$

We have written the quantum number as $(I - 1)$ because we want the lowest eigenvalue to occur when $I = 1$. From Eq. (5-95) for a and Eq. (5-80) for the differential relation between α and z , we determine that

$$a = Y_{\Gamma}^{1/2} \left. \chi'_{\alpha} \right|_{\alpha=\Gamma} . \quad (5-99)$$

The smallest eigenvalues can be determined by solving Eq. (5-96) for Λ_I and substituting E_I from Eq. (5-98) and a from Eq. (5-99) in the result to obtain

$$\Lambda_I = \frac{1}{2} (2I - 1) X_\alpha \Big|_{\alpha=\Gamma} + V_{\min}(\Gamma) \quad (5-100)$$

To determine $V_{\min}(\Gamma)$ we drop the term in braces in Eq. (5-89), use Eq. (5-77) for Y_α , and Eq. (5-76) for X_α to obtain the intermediate result,

$$V_{\min}(\alpha) = \frac{B_\alpha^2 \tilde{n}_1(ss)}{\tilde{n}_1(ss) A_\alpha + B_\alpha} \left(\frac{A_\alpha}{B_\alpha} \right) \quad (5-101)$$

At $\alpha = \Gamma$ the preceding equation for the minimum value of the potential becomes [with the assistance of Eq. (5-91)]:

$$V_{\min}(\Gamma) = \frac{1}{2} X_\alpha \Big|_{\alpha=\Gamma} \quad (5-102)$$

Substitution of the preceding result into Eq. (5-100) yields an equation that can be used to compute approximate values of the smallest eigenvalues:

$$\Lambda_I = I X_\alpha \Big|_{\alpha=\Gamma} \quad (5-103)$$

Another interesting form is obtained by combining Eqs. (5-100) and (5-103):

$$\Lambda_I = 2I V_{\min}(\Gamma) \quad (5-104)$$

The smallest eigenvalue, Λ_1 , can also be related to the Zel'dovich factor [the coefficient of the critical-size cluster evaporation rate in the equation for J , Eq. (5-70)]. From Eq. (5-76) for X_α and Eq. (5-91) for Γ we can prove

$$\left(\ln \frac{A_\alpha}{B_\alpha} \right) \bigg|_{\alpha=\Gamma} = \frac{1}{B_\Gamma} X_\alpha \bigg|_{\alpha=\Gamma} . \quad (5-105)$$

Hence, Λ_1 as a function of the Zel'dovich factor [from Eq. (5-72)] is, with the assistance of the preceding equation,

$$\Lambda_1 = 2\pi B_\Gamma z_\Gamma^2 . \quad (5-106)$$

This result has the same form, but different coefficients of $B_\Gamma z_\Gamma^2$, as several other time constants for establishment of the steady state summarized by Abraham (1974, pp. 99-100). From Eq. (5-69) for J , Eq. (5-105), and Eq. (5-103) for Λ_1 ,

$$J = \left[\frac{\Lambda_1 B_\Gamma}{2\pi} \right]^{1/2} S \frac{\Gamma \tilde{n}_\Gamma(\text{eq})}{V} . \quad (5-107)$$

The monomer depletion time constant as defined by Eq. (5-74) becomes, after substitution of J from Eq. (5-107),

$$\tau^{-1} = \left[\frac{\Lambda_1 B_\Gamma}{2\pi} \right]^{1/2} S^{\Gamma-1} \frac{\tilde{n}_\Gamma(\text{eq})}{\tilde{n}_1(\text{eq})} . \quad (5-108)$$

From the preceding equation it is evident that τ and Λ_1 are related; however, it is not evident that the required condition for validity of Eq. (5-73),

$$\tau \gg \Lambda_1^{-1} , \quad (5-109)$$

is always true if the saturation ratio becomes large. Numerical examples provide the best clue. Abraham (1974, p. 104) quotes typical currents of 10^{12} to $10^{18} \text{ cm}^{-3} \cdot \text{s}^{-1}$ in nozzle experiments. Based on a monomer density of $10^{18} \text{ molecules/cm}^3$, these values correspond to characteristic monomer depletion times of $\tau = 10^6$ to 1.0 s . Numerical values reported in Ch. 10 of this work imply $k_1^{-1} = 10^{-5}$ to 10^{-8} s at $T = 300 \text{ K}$, with the smaller value at the higher saturation ratio S . These numerical values imply that Eq. (5-73) for monomer number density will probably be valid for analyzing most nozzle experiments.

CHAPTER 6

EQUATIONS OF STATE AND TRANSLATIONAL FREE ENERGY

The master equations developed in Ch. 4 were used to compute average quantities that were identified as thermodynamic variables consistent with Euler's equation of thermodynamics. We will prove that simultaneous solution of the master equations for all cluster probabilities and a molecule conservation equation that can be solved for N (the number of clusters) provide enough information (when given a set of densities of states) to calculate a complete set of time-dependent thermodynamic quantities. This result occurs because PV is determined from the distribution of energy levels and because all other quantities are derivable from PV . Eigenenergies for cluster translation states are substituted into the equation for PV and the consequences are analyzed. We find: (1) that we obtain equations for Bose-Einstein condensation when the temperature is near absolute zero and (2) that the kinetic coefficients and equation for PV simplify to a manageable form at temperatures that are higher. Analysis of the equilibrium condition reveals that the single chemical potential that exists in equilibrium is determined by molecule conservation. We analyze that same molecule conservation equation by variation of volume along an isotherm and find that the chemical potential varies with volume and becomes single-valued at a volume less than critical (the saturation volume). The single-value property of the chemical potential implies the formation of a liquid or solid phase. For volumes less than or equal to the saturation volume the chemical potential is equal to the Helmholtz free energy of a molecule bound in an infinite medium; hence, we obtain equations for the

specific saturation volume (and pressure) as a function of Helmholtz free energies and temperatures. We also obtain equations for the heat of evaporation per molecule and per cluster as a function of temperature.

The phase change occurs at a critical volume because the number of available translational energy states is reduced as the volume is decreased until a monomer can be attached to an infinite medium with no free-energy change; the Gibbs free energy is equal to the Helmholtz free energy. If there is no binding energy between molecules the phase change cannot occur until the free energy of a monomer approaches zero. In this case there is only one remaining translational state: the zero momentum state at which Bose-Einstein condensation occurs. The formation of a liquid phase is predicted by our theory in a manner similar to the classical Mayer (1937) theory and the Band (1939a) dissociation theory.

In Ch. 4 we found that an analytic form of the thermodynamic potential PV can be used to determine equations for the thermodynamic variables $\bar{n}_\alpha$ and E_0 . After substituting Eqs. (4-40) through (4-42) into Eq. (4-36) we obtain, for the total energy,

$$E_0 = - \frac{\partial \left(\frac{PV}{kT} \right)}{\partial \left(\frac{1}{kT} \right)} + \sum_{\alpha} G_{\alpha} \bar{n}_{\alpha} \quad , \quad (6-1)$$

and similarly from Eq. (4-37), we obtain, for the average number of clusters of α molecules,

$$\bar{n}_\alpha = \frac{\partial(PV)}{\partial G_\alpha} \quad (6-2)$$

Evaluation of the remaining thermodynamic variables, G_α and S , introduces another quantity, the number distribution $\tilde{n}_\alpha$, because the Gibbs free energy G_α is calculated from Eq. (4-51). The average number $\bar{n}_\alpha$ and the number distribution $\tilde{n}_\alpha$ are related in a complicated way. From Eq. (4-22)

$$\bar{n}_{i\alpha} = \frac{\tilde{n}_{i\alpha}}{1 - \tilde{n}_{i\alpha}} \quad (6-3)$$

where $\bar{n}_\alpha$ is defined by Eq. (4-34) and $\tilde{n}_\alpha$ by Eq. (4-49). After finding PV , $\tilde{n}_\alpha$, E_0 , and G_α , the entropy S can be found from Euler's equation, Eq. (4-38).

The thermodynamic potential PV is a function of all $\bar{n}_{i\alpha}$ [see Eq. (4-47)] which, in turn, are functions of $\tilde{n}_{i\alpha}$ from solutions of the master equation, Eq. (4-61). The master equation involves both number distributions $\tilde{n}_\alpha$ and probabilities P_α which are related by a proportionality constant N ; see Eq. (5-55). Note that solution of the master equation provides only one quantity per cluster size, $\tilde{n}_\alpha$, whereas Eq. (4-47) requires knowledge of a quantity for every energy level, $\tilde{n}_{i\alpha}$. This knowledge is provided on this level of approximation (steady-state solution of the scattering master equation) by the density of state defined by Eq. (4-55). From Eq. (4-52) for $\tilde{n}_{i\alpha}$ and Eq. (4-55):

$$\tilde{n}_{i\alpha} = \tilde{n}_\alpha \rho_{i\alpha} \quad (6-4)$$

The preceding set of equations and variables is not closed because probability is always conserved; hence, summing Eq. (5-55) over α provides no information about N . One more equation is needed. In a manner

analogous to the definition of an energy operator, Eq. (2-57), we can define a molecule number operator as

$$\hat{N} = \sum_{i\alpha} \alpha \hat{n}_{i\alpha} . \quad (6-5)$$

By using the same procedure as that leading to Eq. (4-33) for the average energy, the number of molecules in the system is

$$N = \langle \hat{N} \rangle_R = \sum_{i\alpha} \alpha \bar{n}_{i\alpha} . \quad (6-6)$$

The preceding equation provides the final equation needed for closure of the set equations and variables. From Eqs. (5-55) and (6-4) we find that

$$\tilde{n}_{i\alpha} = N P_{\alpha} \rho_{i\alpha} . \quad (6-7)$$

Hence, substitution of the preceding equation into Eq. (6-3) yields

$$\bar{n}_{i\alpha} = \frac{N P_{\alpha} \rho_{i\alpha}}{1 - N P_{\alpha} \rho_{i\alpha}} . \quad (6-8)$$

The preceding equation implies, from Eq. (6-6), that the total number of molecules is

$$N = N \sum_{i\alpha} \frac{\alpha P_{\alpha} \rho_{i\alpha}}{1 - N P_{\alpha} \rho_{i\alpha}} . \quad (6-9)$$

By using $\tilde{n}_Y$ from Eq. (5-55) in Eq. (4-61), the master equation becomes

$$\begin{aligned} \frac{\partial P_{\delta}}{\partial t} = & \sum_{\gamma=1}^{\infty} \left\{ B_{\delta+\gamma, \gamma} P_{\delta+\gamma} - A_{\delta, \gamma} N P_{\gamma} P_{\delta} \right\} \\ & + \sum_{\gamma=1}^{\delta-1} \left\{ A_{\delta-\gamma, \gamma} N P_{\gamma} P_{\delta-\gamma} - B_{\delta, \gamma} P_{\delta} \right\} . \end{aligned} \quad (6-10)$$

The kinetic coefficients $B_{\alpha, \beta}$ and $A_{\alpha, \beta}$ are functions of $\bar{n}_{i\alpha}$ [see Eqs. (4-57) and (4-60)]; hence, they can be considered as functions of N and P_{α} via Eq. (6-8). Therefore, the two preceding equations, Eqs. (6-9) and (6-10), provide a set of equations that can, in principle, be simultaneously solved for N and all P_{α} as a function of time. Values of N and P_{α} can be substituted into Eqs. (6-8) and (6-3) to find $\bar{n}_{i\alpha}$ and $\tilde{n}_{i\alpha}$, which can be used, in turn, to obtain a complete set of equations of state as a function of time.

For completion of the equation-of-state analysis, the eigenenergies must be determined from the Schrödinger wave equation and the sums over quantum numbers in Eq. (4-47) for PV must be completed to obtain the thermodynamic potential. By using Eq. (6-3) for $\bar{n}_{i\alpha}$ in Eq. (4-47), the thermodynamic potential becomes

$$PV = - kT \sum_{i\alpha} \ln (1 - \tilde{n}_{i\alpha}) . \quad (6-11)$$

From Appendix I we find that the thermodynamic potential can also be written as a sum of Bose functions,

$$PV = kT \sum_{i\alpha} g_1(\tilde{n}_{i\alpha}) = kT \sum_{i\alpha} \sum_j \frac{1}{j} (\tilde{n}_{i\alpha})^j . \quad (6-12)$$

For partial fulfillment of the eigenenergies required by $\tilde{n}_{i\alpha}$ we note that the Hamiltonian for single-particle states is the sum of two terms: (1) $\hat{H}_K$ for the center-of-mass motion of the clusters, and (2) $\hat{H}_I$ for the motion relative to the center of mass:

$$\hat{H}_O = \hat{H}_K + \hat{H}_I \quad . \quad (6-13)$$

The second term involves vibrational and rotational degrees of freedom. The eigenvector can be written as a direct product of translation and internal states:

$$| i\alpha \rangle = | i(I)\alpha, i(K)\alpha \rangle \quad . \quad (6-14)$$

The eigenvalue equations are

$$\hat{H}_K | i(K)\alpha \rangle = \epsilon_{i(K)\alpha} | i(K)\alpha \rangle \quad (6-15)$$

and

$$\hat{H}_I | i(I)\alpha \rangle = \epsilon_{i(I)\alpha} | i(I)\alpha \rangle \quad . \quad (6-16)$$

Equations (6-13) through (6-16) imply

$$\epsilon_{i\alpha} = \epsilon_{i(K)\alpha} + \epsilon_{i(I)\alpha} \quad . \quad (6-17)$$

To find the eigenenergies, $\epsilon_{i(K)\alpha}$, we must transform Eq. (6-15) into a wave equation by methods discussed at the end of Ch. 2. For center-of-mass motion the Hamiltonian operator is

$$\hat{H}_K = \frac{\hat{p}^2}{2 m \alpha} \quad , \quad (6-18)$$

where m is the mass of a single molecule and $\hat{p}$ is the momentum operator. Multiplication of both sides of Eq. (6-15) by the position bra $\langle q |$, using Eq. (6-18) for $\hat{H}_K$, the theorem of Eq. (2-64), and Eq. (2-66) for $\psi_{i(K)\alpha}(q)$ lead to a wave equation for free particles:

$$(\nabla^2 + k_{i(K)\alpha}^2) \psi_{i(K)\alpha}(q) = 0 \quad , \quad (6-19)$$

where we have created the identity

$$k_{i(K)\alpha} \equiv \frac{\sqrt{2 m \alpha \epsilon_{i(K)\alpha}}}{\hbar} \quad (6-20)$$

to define a wave number. Equation (6-19) can be solved by separation of variables,

$$\psi_{i(K)\alpha}(q) = \psi_{\ell\alpha}(x) \psi_{m\alpha}(y) \psi_{n\alpha}(z) \quad , \quad (6-21)$$

where ℓ , m , and n are quantum numbers for eigenenergies of motion in the x , y , and z directions, respectively. The translational wave functions must go to zero at the boundaries of the container whose dimensions are L_x , L_y , and L_z . Substitution of Eq. (6-21) into Eq. (6-19) and imposing the boundary condition leads to the well-known solution:

$$\psi_{i(K)\alpha} = \text{const} \sin(k_x x) \sin(k_y y) \sin(k_z z)$$

$$k_x = \frac{2\pi\ell}{L_x}, \quad k_y = \frac{2\pi m}{L_y}, \quad k_z = \frac{2\pi n}{L_z} \quad (6-22)$$

$$\ell, m, n = 0, \pm 1, \pm 2, \dots$$

$$k_{i(K)\alpha}^2 = k_x^2 + k_y^2 + k_z^2.$$

The eigenenergies from Eqs. (6-20) and (6-22) are

$$\epsilon_{i(K)\alpha} = \epsilon_{\ell mn\alpha} = \frac{h^2}{2m\alpha} \left[\left(\frac{\ell}{L_x} \right)^2 + \left(\frac{m}{L_y} \right)^2 + \left(\frac{n}{L_z} \right)^2 \right]. \quad (6-23)$$

If we define a temporary quantity as

$$Z_{i(I)\alpha} \equiv \tilde{n}_\alpha e^{-(\epsilon_{i(I)\alpha} - F_\alpha)/kT}, \quad (6-24)$$

Eq. (6-4) for $\tilde{n}_{i\alpha}$, Eq. (6-17) for $\epsilon_{i\alpha}$, Eq. (4-55) for $\rho_{i\alpha}$, and Eq. (6-24) for $Z_{i(I)\alpha}$ combine to yield

$$\tilde{n}_{i\alpha} = e^{-\epsilon_{i(K)\alpha}/kT} Z_{i(I)\alpha}. \quad (6-25)$$

Let us define a generalized Helmholtz free energy of translation by

$$F_\alpha^{K(j)} = -kT \ln \sum_{i(K)} e^{-\epsilon_{i(K)\alpha}^j/kT}. \quad (6-26)$$

Then from Eq. (6-12) for PV , Eq. (6-25) for $\tilde{n}_{i\alpha}$, and Eq. (6-26) for $F_{\alpha}^K(j)$ we find the thermodynamic potential

$$PV = kT \sum_j \frac{1}{j} \sum_{i(I)\alpha} \left(z_{i(I)\alpha} \right)^j e^{-F_{\alpha}^K(j)/kT} . \quad (6-27)$$

To evaluate the free-energy term we substitute Eq. (6-23) into Eq. (6-26):

$$F_{\alpha}^K(j) = -kT \ln \sum_{\ell=-\infty}^{\infty} \sum_{m=-\infty}^{\infty} \sum_{n=-\infty}^{\infty} e^{-\frac{h^2 j}{2m\alpha kT} \left[(\ell/L_x)^2 + (m/L_y)^2 + (n/L_z)^2 \right]} \quad (6-28)$$

For closely spaced translational energy levels we can convert the sums in Eq. (6-28) to integrals,

$$\sum_{\ell=-\infty}^{\infty} \longrightarrow \int_{-\infty}^{\infty} d\ell . \quad (6-29)$$

We define a thermal wavelength as

$$\lambda \equiv \frac{h}{\sqrt{2\pi m kT}} \quad (6-30)$$

and the volume available for translational motion as

$$V \equiv L_x L_y L_z . \quad (6-31)$$

The free-energy term is then found by substituting Eqs. (6-29) through (6-31) into Eq. (6-28) and completing the integration:

$$e^{-F_{\alpha}^K(j)/kT} = \frac{V}{\lambda^3} \left(\frac{\alpha}{j}\right)^{3/2} . \quad (6-32)$$

For $j = 1$ we get the ordinary Helmholtz free energy of translation from the previous equation. Substitution of Eq. (6-32) into Eq. (6-27) and using Eq. (I-1) yields the thermodynamic potential

$$PV = kT \sum_{i(I)\alpha} g_1(Z_{i(I)\alpha}) + kT \frac{V}{\lambda^3} \sum_{i(I)\alpha} \alpha^{3/2} g_{5/2}(Z_{i(I)\alpha}) . \quad (6-33)$$

The first term in Eq. (6-33) was added to account for the zero-momentum states ($l = m = n = 0$) that were omitted when the sums in Eq. (6-28) were converted to integrals. The g_1 and $g_{5/2}$ denote Bose functions discussed in Appendix I.

We can use Eq. (4-50) for F_{α} to rewrite the quantity $Z_{i(I)\alpha}$ in an alternative form that employs the Gibbs free energy, i.e.,

$$Z_{i(I)\alpha} = e^{-(\epsilon_{i(I)\alpha} - G_{\alpha})/kT} . \quad (6-34)$$

We use the preceding result and Eqs. (I-5) and (6-33) to find the average number specified by Eq. (6-2):

$$\bar{n}_{\alpha} = \sum_{[i(I)](\alpha)} g_0(Z_{i(I)\alpha}) + \frac{V}{\lambda^3} \sum_{[i(I)](\alpha)} \alpha^{3/2} g_{3/2}(Z_{i(I)\alpha}) . \quad (6-35)$$

The quantity $Z_{i(I)\alpha}$ can be written in a third form by noting that Eq. (6-17) implies that the Helmholtz free energy may be written as the sum of a translational term and an internal term, i.e.,

$$F_{\alpha} = F_{\alpha}^K + F_{\alpha}^I, \quad (6-36)$$

where F_{α}^K is defined by (6-26) with $j = 1$; a similar expression exists for F_{α}^I :

$$F_{\alpha}^I = -kT \ln \sum_{[i(I)](\alpha)} e^{-\epsilon_{i(I)\alpha}/kT} \quad (6-37)$$

If we define a density of internal states as

$$\rho_{i(I)\alpha} = e^{-(\epsilon_{i(I)\alpha} - F_{\alpha}^I)/kT}, \quad (6-38)$$

substitution of Eq. (5-55) for $\tilde{n}_{\alpha}$, Eq. (6-36) for F_{α} , Eq. (6-26) (with $j = 1$) for F_{α}^K , and Eq. (6-38) for $\rho_{i(I)\alpha}$ into Eq. (6-24) yields:

$$Z_{i(I)\alpha} = N P_{\alpha} \rho_{i(I)\alpha} \alpha^{-3/2} \frac{\lambda^3}{V}. \quad (6-39)$$

From Eqs. (6-6) for N and (6-35) for $\bar{n}_{\alpha}$ the molecule conservation equation is

$$N = \sum_{i(I)\alpha} \alpha g_o(Z_{i(I)\alpha}) + \frac{V}{\lambda^3} \sum_{i(I)\alpha} \alpha^{5/2} g_{3/2}(Z_{i(I)\alpha}). \quad (6-40)$$

This equation (with Eqs. (6-38) and (6-39) as intermediaries) and the master equation, Eq. (6-10), provide the means for solving for N and

all P_α when a set of internal energy states is given. Hence, one can obtain a complete set of equations of state at any time, as observed previously. The Gibbs free energy is found by combining Eqs. (6-34) and (6-59) for $Z_{i(I)\alpha}$ and summing the result over $[i(I)](\alpha)$:

$$G_\alpha = F_\alpha^I + kT \ln \left(P_\alpha \frac{N}{V} \alpha^{-3/2} \lambda^3 \right) . \quad (6-41)$$

The total energy can be obtained by application of Eq. (6-1) to Eq. (6-53) and using Appendix I to evaluate the derivative. This last step supplies the last term needed to evaluate the entropy from Euler's equation.

The preceding equations are more precise than needed for solving a homogeneous-nucleation problem. This becomes evident by examining $Z_{i(I)\alpha}$ given by Eq. (6-39). If we define a molecular weight as M and insert numerical values for contrants in Eq. (6-30) the termal wavelength is

$$\lambda(\text{cm}) = \left[\frac{300}{M (\text{g/mole}) T(\text{K})} \right]^{1/2} 1.008 \times 10^{-8} . \quad (6-42)$$

Because $\rho_{i(I)\alpha} < 1$, $P_\alpha < 1$, and $\alpha^{-3/2} < 1$, their product is less than one; hence, for typical gas densities N/V of 10^{18} - 10^{20} molecules/cm³, it can be seen from Eqs. (6-39) and (6-42) that unless $T \ll 300$ K,

$$Z_{i(I)\alpha} \ll 1 , \quad \forall i(I)\alpha . \quad (6-43)$$

The eigenenergies $\epsilon_{i(I)\alpha}$ are all positive; hence, we conclude from Eqs. (6-25) and (6-43) that, unless $T \ll 300$ K,

$$\tilde{n}_{i\alpha} \ll 1 \quad . \quad (6-44)$$

If the condition of Eq. (6-43) holds it is evident from App. I that

$$g_n(Z_{i(I)\alpha}) \approx Z_{i(I)\alpha}, \quad \forall i(I)\alpha, n \quad ; \quad (6-45)$$

and the first terms of Eqs. (6-33) and (6-40) become negligible. However, near absolute zero temperature $Z_{i(I)\alpha}$ may approach its maximum value of unity and the first term of Eq. (6-40) can become dominant. Because of the $\alpha^{-3/2}$ factor in Eq. (6-39) this can only occur for the monomer; hence, only the first term in the sum over α needs to be considered in Eqs. (6-33) and (6-40). The first-term dominance in Eq. (6-40) is an indication that monomers are in the zero-momentum state. This condition is Bose-Einstein condensation. If we consider only the first term in Eq. (6-40) and assume no internal energy states of the monomer, this equation reduces to the starting point of Bose-Einstein condensation theory presented by Huang (1963, Ch. 12). The effects of including the internal energy states of the monomer are considered by Goldstein (1941). If we neglect internal energy states it can be shown from Eq. (6-39) that Bose-Einstein condensation occurs when the space available to a molecule approaches the thermal wave length, i.e., when

$$\left(\frac{V}{\tilde{n}_1} \right)^{1/3} \approx \lambda \quad . \quad (6-46)$$

A more precise form of Eq. (6-46) is given by Huang (1963, p. 263).

Our work is concerned with condensation by nucleation; hence, we will make the approximation implied by Eqs. (6-43) and (6-44). In this approximation we find, after substituting Eq. (6-45) into Eq. (6-35) and using Eq. (6-39) for $Z_{i(I)\alpha}$, that:

$$\bar{n}_{\alpha} \approx N P_{\alpha} \quad . \quad (6-47)$$

Upon comparing Eqs. (5-55) and (6-47) we conclude

$$\tilde{n}_{\alpha} \approx \bar{n}_{\alpha} \quad . \quad (6-48)$$

From Eqs. (6-6) and (6-48), the conservation of molecules equation, Eq. (6-9), becomes

$$N = N \sum_{\alpha} \alpha P_{\alpha} \quad . \quad (6-49)$$

Simultaneous solution of the preceding equation and of the master equation, Eq. (6-10) provides N and all P_{α} . Note that the approximation implied by Eq. (6-44) allows us to take $(1 + \bar{n}_{i\alpha}) \approx 1$ in the calculation of the kinetic coefficients $A_{\alpha,\beta}$ and $B_{\alpha,\beta}$; hence, they can be considered to be constant in time if the temperature is constant. The thermodynamic potential can be obtained by substituting Eq. (6-45) for $g_{5/2}(Z_{i(I)\alpha})$ into Eq. (6-33) and using the approximation of Eq. (6-43):

$$PV = N kT \quad . \quad (6-50)$$

By summing Eq. (6-47) over α we find the number of clusters is

$$N = \sum_{\alpha} \bar{n}_{\alpha} \quad , \quad (6-51)$$

where $\bar{n}_{\alpha}$ is found by combining Eq. (4-50) and Eq. (6-48) to obtain

$$\bar{n}_{\alpha} = e^{-(F_{\alpha} - G_{\alpha})/kT} \quad . \quad (6-52)$$

From Eqs. (6-50) through (6-52) we see that Eq. (6-1) for the total energy is equivalent to

$$E_o = \sum_{\alpha} \frac{\partial \left(\frac{F_{\alpha}}{kT} \right)}{\partial \left(\frac{1}{kT} \right)} \bar{n}_{\alpha} \quad . \quad (6-53)$$

If we define an internal energy as

$$E_{\alpha}^I = \frac{\partial \left(\frac{F_{\alpha}^I}{kT} \right)}{\partial \left(\frac{1}{kT} \right)} \quad , \quad (6-54)$$

we can use Eq. (6-36) for F_{α} and Eq. (6-32) for F_{α}^K , Eq. (6-53) for E_o , Eq. (6-50) for N , and (6-47) for $\bar{n}_{\alpha}$ to prove:

$$E_o = N \left\{ \frac{3}{2} kT + \sum_{\alpha} E_{\alpha}^I P_{\alpha} \right\} \quad . \quad (6-55)$$

By using Eq. (6-47) we can rewrite the Euler equation, Eq. (4-39), in terms of the probability and number of clusters:

$$S = \frac{1}{T} \left\{ E_o + PV - N \sum_{\alpha} P_{\alpha} G_{\alpha} \right\} \quad . \quad (6-56)$$

Given solutions of the master equation and Eq. (6-47) for N and P_α ; Eq. (6-50) for PV , (6-55) for E_α , (6-41) for G_α , and (6-56) for S constitute a complete set of equations of state at any time. Additionally, we have the number distribution of clusters from Eqs. (6-52), (6-36), and (6-32):

$$\bar{n}_\alpha = \frac{V}{\lambda^3} \alpha^{3/2} e^{-(F_\alpha^I - G_\alpha)/kT} \quad (6-57)$$

The previous formulae for equations of state are based on distribution functions valid at any time, including $t = \infty$, providing that molecules are conserved according to Eq. (6-49). One infinite-time distribution, the equilibrium distribution, is characterized by the existence of a single Gibbs free energy, μ , that is denoted the chemical potential. The Gibbs free energy in equilibrium is given by Eq. (5-32). Upon substitution of Eq. (5-32) into Eq. (6-57) the equilibrium distribution of clusters becomes

$$\bar{n}_\alpha(\text{eq}) = \frac{V}{\lambda^3} \alpha^{3/2} e^{-(F_\alpha^I - \mu\alpha)/kT} \quad (6-58)$$

In equilibrium we no longer have a set of differential equations to determine all the $\bar{n}_\alpha$ [or G_α , see Eq. (6-57)]; hence, the distribution is a function of only one parameter, μ , as it must be. The parameter μ is directly related to the usual molecule conservation parameter N via Eqs. (6-51) and (6-58). Instead of calculating N as an intermediate step we find μ by solving the implicit molecule-conservation equation that results from substitution of Eqs. (6-58) and (6-47) into Eq. (6-49), i.e.,

$$N = \frac{V}{\lambda^3} \sum_{\alpha} \alpha^{5/2} e^{-(F_{\alpha}^I - \mu\alpha)/kT} \quad (6-59)$$

From Eqs. (6-58) and (6-51) the number of clusters in the equilibrium state is

$$N(\text{eq}) = \frac{V}{\lambda^3} \sum_{\alpha} \alpha^{3/2} e^{-(F_{\alpha}^I - \mu\alpha)/kT} ; \quad (6-60)$$

hence, through Eqs. (6-50) for PV and (6-60) for N , the complete equilibrium equation of state can be determined.

The condition for convergence of the series summation in Eq. (6-59) can be determined by the ratio test. For convergence it is required that

$$\lim_{\alpha \rightarrow \infty} \left(\frac{\alpha+1}{\alpha} \right)^{5/2} e^{-(F_{\alpha+1}^I - F_{\alpha}^I - \mu)/kT} < 1 \quad (6-61)$$

The preceding equation implies convergence if

$$\mu < \lim_{\alpha \rightarrow \infty} (F_{\alpha+1}^I - F_{\alpha}^I) \quad (6-62)$$

The quantity on the right side of Eq. (6-62) is the Helmholtz free energy per molecule for a molecule bound in an infinite medium f_{∞}^I where

$$f_{\infty}^I = \lim_{\alpha \rightarrow \infty} \frac{F_{\alpha}^I}{\alpha} \quad , \quad (6-63)$$

and f_{α} is defined by Eq. (5-37). Hence, the condition for convergence can be simply written as

$$\mu < f_{\alpha}^I \quad . \quad (6-64)$$

The series diverges if $\mu > f_{\alpha}^I$ and the ratio test fails if $\mu = f_{\alpha}^I$.

The same analysis applies to the series summation in Eq. (6-60).

If we define specific volume $v(\mu)$ as the volume per molecule, then the volume available to a gas of clusters is

$$V = N v(\mu) \quad . \quad (6-65)$$

We obtain $v(\mu)$ from Eqs. (6-59) for N , (6-65) for V , and (5-37) for f_{α}^I :

$$v(\mu) = \frac{\lambda^3}{\sum_{\alpha} \alpha^{5/2} e^{-(f_{\alpha}^I - \mu)\alpha/kT}} \quad . \quad (6-66)$$

From Eq. (6-66) we see that if $\mu \geq f_{\infty}^I$, the series summation diverges and $v(\mu) = 0$. This causes some difficulty with Eq. (6-65); i.e., the volume (an externally controlled quantity) either discontinuously drops to zero at $\mu = f_{\infty}^I$ or, if we try to solve for N , we must divide by a quantity that can have a zero value. Following a method similar to Dirac's (1958, p. 61), the result of division of zero by zero is defined in terms of a Kronecker delta function; i.e., from Eq. (6-65),

$$\frac{N v(\mu) - V}{v(\mu)} = C(V) \delta(\mu, f_{\infty}^I) \quad , \quad (6-67)$$

where $C(V)$ is a quantity to be determined, and the Kronecker delta function is

$$\delta(x, y) = \begin{cases} 1, & x = y \\ 0, & x \neq y \end{cases} . \quad (6-68)$$

From Eq. (6-67)

$$N = \frac{V}{v(\mu)} + C(V) \delta(f_{\infty}^I, \mu) . \quad (6-69)$$

When numerically computing the sum in Eq. (6-66) with $\mu = f_{\infty}$ the last term at $\alpha = \infty$ is never reached; hence, for practical purposes the series converges and Eq. (6-66) can be employed for $\mu \leq f_{\infty}^I$. The physical interpretation of Eq. (6-69) is that the first term,

$$N_g = \frac{V}{v(\mu)} , \quad (6-70)$$

is the number of molecules in the gas phase and the second term,

$$N_{\ell} = C(V) \delta(f_{\infty}^I, \mu) , \quad (6-71)$$

is the number of molecules in the liquid or solid, phase.

To find $C(V)$ we evaluate N from Eq. (6-69) at $\mu = f_{\infty}^I$. Substituting the result into Eq. (6-71) yields,

$$N_{\ell} = \left\{ N - \frac{V}{v(f_{\infty}^I)} \right\} \delta(f_{\infty}^I, \mu) . \quad (6-72)$$

The critical volume at which N_{ℓ} first appears is called the saturation volume:

$$V_s = N v(f_{\infty}^I) \quad . \quad (6-73)$$

Combining Eqs. (6-72) and (6-73) gives the number of molecules in the liquid phase as

$$N_{\ell} = N \left(1 - \frac{V}{V_s}\right) \delta(\mu, f_{\infty}^I) \quad . \quad (6-74)$$

The remaining molecules are in the gas phase, i.e., the total number of molecules is

$$N = N_g + N_{\ell} \quad , \quad (6-75)$$

where N_g is given by Eq. (6-70) and N_{ℓ} either by Eq. (6-72) or Eq. (6-74). The formation of the liquid or solid phase is consistent with the steady-state analysis, which predicts a constant probability current toward an infinite-size cluster if the saturation ratio S is greater than one.

Analysis of Eqs. (6-59) and (6-66) by variation of volume along an isotherm indicates the shape of a μ versus V curve. If the volume is very large, v must also be large according to Eq. (6-65) because N is a fixed number. The specific volume v can only become large by allowing μ to be negative and have large absolute value. If this is the case, only the first term of the sum in Eq. (6-59) will contribute and we obtain, for "large" volume,

$$\mu = - kT \ln \left(\frac{V}{N \lambda^3} \right) . \quad (6-76)$$

As the volume is decreased, the magnitude of μ can decrease by Eq. (6-76) or more accurately by Eq. (6-59), until $\mu = f_{\infty}^I$. Further decreases in V allow no further change in μ by Eq. (6-64); hence, the number of molecules in the gas phase decreases in direct proportion to V from Eq. (6-70) and the number of liquid molecules has to increase to keep N fixed. The transition point from μ given by the upper limit of Eq. (6-64) to μ given by Eq. (6-59) [or approximately by Eq. (6-76)] occurs at $V = V_s$, the saturation volume. The result of this analysis is a sketch of μ versus V along an isotherm as shown in Fig. 1.

Evaluation of μ as a function of volume V from Eq. (6-59) allows evaluation of P from Eq. (6-50). This is most easily accomplished by noting that,

$$\frac{\partial P}{\partial V} = \frac{\partial P}{\partial \mu} \frac{\partial \mu}{\partial V} = \frac{N}{V} \frac{\partial \mu}{\partial V} , \quad (6-77)$$

where the second step follows from Eqs. (6-50) and (6-60). For $V < V_s$, $\frac{\partial \mu}{\partial V} = 0$ (see Fig. 1); hence, P is constant in this region. This value of P is labeled $P_s(T)$. For $V > V_s$ we use Eq. (6-76) for μ and Eq. (6-77) for $\frac{\partial P}{\partial V}$; solve the resulting differential equation and obtain the perfect gas law,

$$PV = N k T . \quad (6-78)$$

This result could also be obtained in a less formal way by noting that, for large "volume", only the first term of the sums in Eqs. (6-59) and

Figure 1

Schematic of chemical potential $\mu(T,V)$ as a function of volume. The upper limit of Eq. (6-64) describes μ for $V < V_s$ and Eq. (6-76) describes μ for $V \gg V_s$.

(6-60) contributes. Equation (6-78) is consistent with Eq. (6-50) because $N \rightarrow N$ when V is large, i.e., when the number of clusters is equal to the number of molecules at very large volume. Near $V = V_s$, it is likely that $N < N$; hence, there is some departure from the straight-line-behavior (on log-log plot) predicted by the perfect gas equation of state, Eq. (6-78). From the above considerations, we have plotted a schematic P versus V curve shown in Fig. 2.

The specific volume, $v_s = V/N$, and the pressure, P_s , at the conditions where liquid or solid first appears can be measured. The saturation volume is the value of v from Eq. (6-66) where $\mu = f_\infty^I$:

$$v_s(T) = \frac{\lambda^3}{\sum_{\alpha} \alpha^{5/2} e^{-(f_\alpha^I - f_\infty^I)\alpha/kT}} \quad (6-79)$$

Similarly, the saturation pressure is

$$P_s(T) = \frac{kT}{\lambda^3} \sum_{\alpha} \alpha^{3/2} e^{-(f_\alpha^I - f_\infty^I)\alpha/kT} \quad (6-80)$$

If the above equations accurately describe the measured data over a temperature range that includes some clustering, we have assurances that: (1) the basic theory is correct, (2) we have a proper method for identifying the saturation volume, and (3) the particular method used to calculate the free energies is correct.

The cluster fraction in terms of measureable macroscopic quantities can be found from Eqs. (6-50), (6-60), and (6-59):

$$\frac{N}{N} = \frac{Pv}{kT} \quad (6-81)$$

Figure 2

Schematic of pressure $P(T,V)$ as a function of volume. Constant value for $V < V_s$ is the saturation pressure. The functional form at large volume is given by Eq. (6-78).

Along the coexistence line,

$$\frac{N_s}{N} = \frac{P_s v_s}{kT} = \frac{\sum_{\alpha} \alpha^{3/2} e^{-(f_{\alpha}^I - f_{\infty}^I)\alpha/kT}}{\sum_{\alpha} \alpha^{5/2} e^{-(f_{\alpha}^I - f_{\infty}^I)\alpha/kT}} \quad (6-82)$$

Our method predicts clustering if $N/N < 1$.

From Eqs. (6-79) and (6-80) it can be seen that the coexistence-line curves $v_s(T)$ and $P_s(T)$ are functions of the internal Helmholtz free energies (of all clusters) which, in turn, are functions of the temperature. Because the nucleation rates are strong functions of the Helmholtz free energies [see Eq. (5-61)], much of the success in predicting droplet formation rates will depend to a large extent on how well our calculations of internal free energies predict the coexistence-line curves. Methods of finding internal free energies will be explored in Ch. 7.

In addition to the coexistence-line quantities $v_s(T)$ and $P_s(T)$, we can also calculate the slope of the coexistence-line pressure to obtain functions that are measured as heats of vaporization. To study the heat vaporization, we use the Clausius-Clapeyron equation that describes the change in saturation pressure with temperature. The Clausius-Clapeyron equation is easily derived from thermodynamics [see for example Sears (1956, p. 119, p. 163)]:

$$\frac{dP_s}{dT} = \frac{L}{T (V_g - V_l)} \quad (6-83)$$

In the preceding equation, V_g is the volume occupied by the gas and V_l is the volume occupied by the liquid. The heat released when the system

is changed from liquid to gas at constant temperature is

$$L = T (S_g - S_\ell) ,$$

where S_g is the entropy of the gas and S_ℓ is the entropy of the liquid. Solution of Eq. (6-83) requires an equation of state, which can be obtained from Eq. (6-50). In the derivation of Eq. (6-50) the boundary conditions for the translational wave functions define the volume; hence, the volume in this equation is the volume available to the gas. At the saturation line, we obtain from Eq. (6-50)

$$P_s V_g = N_s kT . \quad (6-84)$$

The subscript s on N implies that this quantity is to be computed from Eq. (6-60) with $\mu = f_\infty^I$. Let $\ell_m = L/N$ be the heat of vaporization per molecule, then substitution of Eq. (6-84) into Eq. (6-83) yields

$$\ell_m(T) = -k \left(1 - \frac{v_\ell}{v_g} \right) \frac{d(\ln P_s)}{d\left(\frac{1}{T}\right)} \frac{N_s}{N} . \quad (6-85)$$

Except for temperatures near the critical temperatures T_c the specific volume of the liquid is much less than the specific volume of the gas ($v_\ell \ll v_g$). The clustering fraction, N_s/N , is the number of clusters per molecule; hence, we can define heat of vaporization per cluster as

$$\ell_c(T) = -k \frac{d(\ln P_s)}{d\left(\frac{1}{T}\right)} . \quad (6-86)$$

At low temperature we expect to have $\ell_m(T) \approx \ell_c(T)$ because only the first terms in the sums for N/N from Eq. (6-82) will contribute and we will have $N \approx N$. The two heat-of-vaporization curves will diverge as the temperature is increased toward the critical temperature and clustering effects become important. Experimental values of $\ell_c(T)$ to be compared with Eq. (6-85) are available for some materials and experimental values of $\ell_m(T)$ can be obtained by numerical differentiation of saturation-line pressure data. An analytic form of $\ell_c(T)$ is obtained by differentiation of Eq. (6-80). If we define

$$\Delta F_{\alpha}^I = F_{\alpha}^I - \alpha f_{\alpha}^I, \quad (6-87)$$

the result is

$$\ell_c(T) = \frac{5}{2} kT + \Delta E^I, \quad (6-88)$$

where

$$\Delta E^I = \frac{\sum_{\alpha} \alpha^{3/2} \Delta E_{\alpha}^I e^{-\Delta F_{\alpha}^I/kT}}{\sum_{\alpha} \alpha^{3/2} e^{-\Delta F_{\alpha}^I/kT}} \quad (6-89)$$

and

$$\Delta E_{\alpha}^I = E_{\alpha}^I - \alpha \varepsilon_{\infty}^I = \frac{\partial \left(\frac{\Delta F_{\alpha}^I}{T} \right)}{\partial \left(\frac{1}{T} \right)}. \quad (6-90)$$

The heat of vaporization per cluster consists of three terms: (1) $\frac{3}{2} kT$, the change in translation energy as the cluster is released from

the infinite medium; (2) kT , the Pv work due to change in specific volume; and (3) ΔE^I , the change in internal energy consisting of rotational and vibrational terms.

CHAPTER 7

ROTATIONAL AND VIBRATIONAL FREE ENERGY

From the development of Chs. 5 and 6 it is apparent that the calculation of equations of state and nucleation rates requires a practical method for calculating the internal Helmholtz free energy of clusters of all sizes (including the infinite medium), or, more precisely, the free-energy difference ($f_{\alpha}^I - f_{\infty}^I$). Other nucleation theories also depend on a Helmholtz free-energy difference, often incorrectly referred to as a Gibbs free-energy difference. The classical nucleation theory, see for example McDonald (1962,1963), relies on surface tension data to provide the required free-energy difference. The surface tension is an infinite-medium measurement; hence, it alone does not provide the necessary information about small clusters. Also, the classical nucleation theory does not include the translational and rotational free energy of clusters. Attempts by Lothe and Pound (1962) to correct the classical nucleation theory, by including translational and rotational free energy, and by accounting for missing degrees of freedom in vibrational free energy at small cluster sizes, have produced a theory that differs both from the classical theory (by 17 orders of magnitude in the nucleation rate) and from experiments; see for example Abraham (1974, p. 165). We propose an alternative method of calculating cluster free energies.

The Helmholtz free energy for internal states of a cluster of molecules is given by Eq. (6-37). The required data are a set of eigenenergies $\epsilon_{i(I)\alpha}$, that can, in principle, be obtained either by solving Schrödinger's wave equation or from spectroscopic measurements. This chapter will be concerned with developing methods for calculating the Helmholtz free

energies of clusters from approximate analytic solutions of the Schrödinger wave equation. For our development, we neglect the coupling between rotational and vibrational energy and write the internal energy of a cluster of molecules as the sum of a rotational free energy, a vibrational free energy, and a constant term that defines the energy at $T = 0$. Well-known methods of calculating the rotational free energy are reviewed. To calculate the vibrational free energy, we apply the Debye approximation to clusters of molecules. The Debye approximation is normally applied to solid crystals; however, because sound waves exist also in liquids, the approximation is applicable to this state if provision is made for anharmonic effects. This point is discussed by Huang (1963, p. 261). To illustrate how the cluster Hamiltonian yields a vibrational free energy, we review the development of the Debye approximation. An anharmonic correction term that allows extension of the Debye theory to liquids is included in the development through perturbation theory in a classical statistical-mechanics analysis. Because the Debye temperature depends on molecule separation and because surface molecules can be expected to be more widely separated than interior molecules (they are bound in a different potential well), we propose to divide the clusters into two classes of molecules: (1) surface molecules and (2) interior molecules, with a different Debye temperature and binding energy for each. We develop a method for calculating the number of surface molecules in each cluster and propose to use a function introduced by Freund and Bauer (1977) for the variation of binding energy of surface molecules with cluster size. The difference in vibrational free energy between surface molecules and interior molecules of large clusters is directly related to the surface tension, an extensively measured quantity.

Let Q_α be the partition function for a cluster of α molecules. The Helmholtz free energy for this cluster is

$$F_\alpha^I = -kT \ln Q_\alpha \quad , \quad (7-1)$$

where F_α^I is defined by Eq. (6-37). The Hamiltonian for internal motion of a cluster is

$$H_I = \frac{1}{2} \sum_{j=1}^{\alpha} m_j \left(\vec{v}_j^I \right)^2 + V_I \quad , \quad (7-2)$$

where the subscript j identifies particles (molecules or atoms) of a cluster of α molecules. The velocity relative to center-of-mass motion is $\vec{v}_j^I$ and the potential energy of molecules bound in a cluster is V_I . If there were no interaction potential in Eq. (7-2), classical analysis tells us that all motion is in the form of angular velocity about the center of mass; however, the internal potential allows additional vibrational motion of each particle in the cluster about an average position that may be rotating about the center of mass. Hence, we should write the internal velocity as

$$\vec{v}_i^I = \vec{v}_i^R + \vec{v}_i^V \quad . \quad (7-3)$$

When $\vec{v}_i^I$ is squared, a cross term involving the cosine of the angle between the rotational velocity $\vec{v}_i^R$ and $\vec{v}_i^V$ develops. Because the two velocities are expected to be largely different, there will be several vibrational cycles per rotational cycle; a time average of the cross term over a period of rotation would be essentially zero. After neglecting the cross term we can write the internal Hamiltonian as the sum of a rotational term and a vibrational term, i.e.,

$$H_I = H_R + H_V \quad , \quad (7-4)$$

$$H_R = \frac{1}{2} \sum_{i=1}^{\alpha} m_i \left(\frac{\dot{R}}{v_i} \right)^2 \quad , \quad (7-5)$$

and

$$H_V = \frac{1}{2} \sum_{i=1}^{\alpha} m_i \left(\frac{\dot{V}}{v_i} \right)^2 + V_I \quad . \quad (7-6)$$

This division of the Hamiltonian is essentially the Born-Oppenheimer approximation in molecular physics. Effects of rotational-vibrational coupling have been estimated by McGinty (1971) and found to be negligible.

In operator form, Eq. (7-4) becomes

$$\hat{H}_I = \hat{H}_R + \hat{H}_V \quad . \quad (7-7)$$

The eigenvector for the internal states is

$$|i(I)\alpha\rangle = |i(R)\alpha, i(V)\alpha\rangle \quad ; \quad (7-8)$$

hence, by operating on Eq. (7-8) with $\hat{H}_I$ from Eq. (7-7) we obtain two Schrödinger equations:

$$H_R |i(R)\alpha\rangle = \epsilon_{i(R)\alpha} |i(R)\alpha\rangle \quad , \quad (7-9)$$

$$\hat{H}_V |i(V)\alpha\rangle = \epsilon_{i(V)\alpha} |i(V)\alpha\rangle \quad , \quad (7-10)$$

and thus the energy for the internal states is

$$\epsilon_{i(I)\alpha} = \epsilon_{i(R)\alpha} + \epsilon_{i(V)\alpha} \quad . \quad (7-11)$$

For certain types of internal motion potentials that may be included in H_V (for example, the harmonic oscillator potential), there is no defined binding energy. In this case the location of the bottom of the potential well is arbitrary and we must add a constant to the right side of Eq. (7-11) to define a reference point for the eigenenergy when $T = 0$; i.e., we replace Eq. (7-11) by

$$\epsilon_{i(I)\alpha} = \epsilon_{i(R)\alpha} + \epsilon_{i(V)\alpha} - W_\alpha \quad (7-12)$$

The sum in Eq. (6-37) is over states. Some of the states may be degenerate, i.e., the same energy level may represent two or more states. If we sum over energy levels instead of states we must include a degeneracy factor. By combining Eq. (7-1) for Q_α , Eq. (6-37) for F_α^I , Eq. (7-12) for $\epsilon_{i(I)\alpha}$, and summing over energy levels instead of states the partition function for a cluster of α molecules is

$$Q_\alpha^I = e^{W_\alpha/kT} \sum_{i(R)} d_{i(R)} e^{-\epsilon_{i(R)\alpha}/kT} \sum_{i(V)} d_{i(V)} e^{-\epsilon_{i(V)\alpha}/kT} \quad (7-13)$$

The $d_{i(R)}$ and $d_{i(V)}$ terms are densities of states for rotation and vibration, respectively. If we define a rotational partition function as

$$Q_\alpha^R = \sum_{i(R)} d_{i(R)} e^{-\epsilon_{i(R)\alpha}/kT} \quad (7-14)$$

and a vibrational partition function as

$$Q_\alpha^V = \sum_{i(V)} d_{i(V)} e^{-\epsilon_{i(V)\alpha}/kT} \quad (7-15)$$

we may write the partition function for internal states, Eq. (7-13), as a product:

$$Q_{\alpha}^I = e^{W_{\alpha}/kT} Q_{\alpha}^R Q_{\alpha}^V . \quad (7-16)$$

For a free energy of rotation defined by

$$F_{\alpha}^R = -kT \ln Q_{\alpha}^R , \quad (7-17)$$

and a free energy of vibration defined by

$$F_{\alpha}^V = -kT \ln Q_{\alpha}^V , \quad (7-18)$$

the internal free energy from Eqs. (7-1), (7-17) and (7-18) is

$$F_{\alpha}^I = -W_{\alpha} + F_{\alpha}^R + F_{\alpha}^V . \quad (7-19)$$

If we define an angular velocity $\vec{\omega}$ by

$$\vec{v}_i^R = \vec{r}_i \times \vec{\omega} \quad (7-20)$$

and an angular momentum as

$$\vec{L} = \sum_i m_i \vec{r}_i \times \vec{v}_i^R , \quad (7-21)$$

the Hamiltonian for rotation, Eq. (7-5), becomes

$$H_R = \frac{1}{2} \vec{\omega} \cdot \vec{L} \quad (7-22)$$

Goldstein (1950, p. 152) has proven that a suitable choice of rotational axes can be found such that the inertia tensor defined by

$$\vec{I} \cdot \vec{\omega} = \vec{L}$$

is diagonal so that we may write the rotational Hamiltonian as

$$H_R = \frac{L_x^2}{I_A} + \frac{L_y^2}{I_B} + \frac{L_z^2}{I_C} \quad (7-23)$$

The terms I_A , I_B , and I_C are moments of inertia about the principal axes of rotation for the diagonalized rotation tensor, and L_x is a Cartesian component of the molecular angular momentum in the molecule-fixed frame:

$$L_x = yp_x - zp_y, \quad L_y = zp_x - xp_z, \quad L_z = xp_y - yp_x \quad (7-24)$$

We can use Eq. (2-64) to find the required Hamiltonian operator for a Schrödinger wave equation by letting

$$L_x \rightarrow \frac{\hbar}{i} \left(y \frac{\partial}{\partial x} - z \frac{\partial}{\partial y} \right), \quad \text{etc.}, \quad (7-25)$$

in Eq. (7-23) to convert H_R to a wave-equation operator. When two or more of the moments of inertia are the same, a change to spherical coordinates yields a differential equation that can be solved in closed form.

To obtain eigenenergies and degeneracy factors for the rotational partition function we may solve the Schrödinger wave equation, Eq. (2-68) [with Hamiltonian operator given by Eqs. (7-23) and (7-25)], in the rigid rotator approximation for four different types of rotators. To summarize the results we list the partition functions as given in several texts [see, for example, Godnev (1956)] as follows:

linear dimer of diatomic molecule,

$$Q^R = \sum_{J=0}^{\infty} (2J+1) e^{-\frac{\hbar^2}{2I_B} J(J+1)/kT} ; \quad (7-26)$$

symmetric top,

$$Q^R = \sum_{J=0}^{\infty} \sum_{K=-J}^J (2J+1) e^{-\frac{\hbar^2}{2} \left\{ \frac{J(J+1)}{I_B} + K^2 \left(\frac{1}{I_A} - \frac{1}{I_B} \right) \right\} /kT} ; \quad (7-27)$$

asymmetrical rotator,

$$Q^R = \sum_{J=0}^{\infty} \sum_{K_{-1}} \sum_{K_{+1}} (2J+1) e^{-E(J, K_{-1}, K_{+1})/kT} ; \quad (7-28)$$

accidentally spherical top,

$$Q^R = \sum_{J=0}^{\infty} (2J+1)^2 e^{-\frac{\hbar^2}{2I} J(J+1)/kT} . \quad (7-29)$$

In the preceding equations, J is the principal angular momentum quantum number; K is the quantum number for the z component of the angular momentum; and I_A , I_B and I_C are moments of inertia about principal axes of rotation, for example:

$$I_B = \sum_i x_i m_i^2 , \quad (7-30)$$

where x_i are distances along the axis from the center of mass to the i^{th} mass, m_i . There is no formula for the eigenenergy of the asymmetrical rotator in terms of quantum numbers; hence, we have written the eigenenergy as a symbolic function of three quantum numbers. The quantum numbers, K_{-1} and K_{+1} , are explained by Tinkham (1964, p. 256). Other parameters that are frequently used instead of the moment of inertia are the rotational constants:

$$A = \frac{h}{4\pi c I_A}, \quad B = \frac{h}{4\pi c I_B}, \quad C = \frac{h}{4\pi c I_C}, \quad (7-31)$$

where c is the speed of light.

Analytic forms of partition functions, Eqs. (7-27) through (7-29), can be found by converting the summations to integrals [see Godnev (1956)]. In terms of rotational constants the results are

$$Q^R = \frac{kT}{Bhc} \quad (7-32)$$

for the linear dimer or diatomic molecule, and

$$Q^R = \sqrt{\frac{\pi}{ABC} \left(\frac{kT}{hc} \right)^3} \quad (7-33)$$

for all other rotations. For certain molecules that have identical atoms it may be necessary to divide the preceding partition functions by a symmetry number σ as discussed by Herzberg (1945, p. 508). If we define rotational temperature as

$$T_{\alpha}^R(K) \equiv 0.9823 \left[A(\text{cm}^{-1}) B(\text{cm}^{-1}) C(\text{cm}^{-1}) \right]^{1/3}, \quad (7-34)$$

we can combine Eqs. (7-33), (7-34), and (7-17); and add a symmetry-number free energy to obtain the Helmholtz free energy of rotation for a cluster of α molecules:

$$F_{\alpha}^R = \frac{3}{2} kT \ln \left(\frac{T_{\alpha}^R}{T} \right) + kT \ln \sigma(\alpha) \quad (7-35)$$

For cases where the rotational constants are available the rotational temperature can be computed directly from Eq. (7-34). If the configuration of the cluster is given, the moment of inertia can be computed from Eq. (7-30), and this result can be substituted into Eq. (7-31) to obtain the rotational constants. For large clusters, configuration data will not be available; however, in that case, the cluster can be considered a uniform sphere. The moment of inertia for a uniform sphere is

$$I = \frac{8\pi}{15} \rho R^5, \quad (7-36)$$

where ρ is the density and R is the radius. A large cluster of molecules will be uniform and will have an average density about equal to the solid or liquid density; hence,

$$R_{\alpha} \approx \left(\frac{3m\alpha}{4\pi\rho} \right)^{1/3} \quad (7-37)$$

By combining Eq. (7-34) (with $A = B = C$) for T_{α}^R , Eq. (7-37) for R_{α} , and using Avogadro's number we obtain for the rotational temperature of a large cluster

$$T_{\alpha}^R = T \alpha^{-5/3}, \quad (7-38)$$

where the proportionality constant is

$$T^R(K) \equiv 76.73 \left[\frac{\rho(g/cm^3)}{M(g/mole)} \right]^{1/3} . \quad (7-39)$$

The vibrational Hamiltonian given by Eq. (7-6) is the sum of a kinetic term,

$$T_V = \frac{1}{2} \sum_{i=1}^D m_i \dot{q}_i^2 , \quad (7-40)$$

and of a potential term, $V_I(q_1, q_2, \dots, q_D)$, where the q_i 's are generalized coordinates and $\dot{q}_i$'s are the velocities that are the conjugate variables in the Lagrangian formalism, i.e.,

$$H_V = T_V + V_V . \quad (7-41)$$

The sum over i extends to D , the number of vibrational degrees of freedom. The total number of degrees of freedom available to a cluster is $3p$, where p is the number of particles that can move independently. We have already accounted for six degrees of freedom per cluster (except for certain special cases that have only two axes of rotation) by allowing three degrees of freedom for translation and three degrees of freedom for rotation. We will consider $D = 3p-6$ for the present, with p to be determined on an individual cluster basis and the temperature. For example, if the atoms of the molecules are rigidly bound together, $p = \alpha$, where α is the number of molecules in the cluster.

For small oscillatory motion about an equilibrium value, q_{oi} , the generalized coordinates can be written as

$$q_i = q_{oi} + \eta_i , \quad (7-42)$$

where r_{q_i} is a small displacement of q_i . Second-order Taylor series expansion of T_V and V_V produces the following results [Goldstein (1950, Ch. 10)].

$$T_V = \frac{1}{2} \sum_{jk} \dot{\eta}_j T_{jk} \dot{\eta}_k , \quad (7-43)$$

$$V_V = \frac{1}{2} \sum_{jk} \eta_j V_{jk} \eta_k , \quad (7-44)$$

where

$$T_{jk} = \sum_i m_i \frac{\partial \vec{r}_i}{\partial q_j} \cdot \frac{\partial \vec{r}_i}{\partial q_k} , \quad (7-45)$$

$$V_{jk} = \frac{\partial^2 V(q)}{\partial q_j \partial q_k} . \quad (7-46)$$

In the preceding, m_i is the mass of the i^{th} particle and $\vec{r}_i$ is its position relative to the center of mass. Goldstein (1950, Ch. 10) presents the procedure for finding the coordinate system where matrices $T \sim T_{jk}$ and $V \sim V_{jk}$ are simultaneously diagonal. The matrix of eigenvectors for the transformation is $\underline{a} \sim a_{ij}$ and the eigenvalues are ω_i^2 . The generalized coordinates in the new coordinate system are ζ_i . The matrix of eigenvectors provides the coordinate transformation, i.e.,

$$\eta_i = \sum_j a_{ij} \zeta_j . \quad (7-47)$$

In the new coordinate system:

$$T_V^O = \frac{1}{2} \sum_i \dot{\zeta}_i^2 \quad , \quad (7-48)$$

$$V_V^O = \frac{1}{2} \sum_i \omega_i^2 \zeta_i^2 \quad . \quad (7-49)$$

The vibrational Lagrangian for a cluster is

$$L_V^O = T_V^O - V_V^O = \frac{1}{2} \sum_i \left(\dot{\zeta}_i^2 - \omega_i^2 \zeta_i^2 \right) . \quad (7-50)$$

From the preceding we obtain the generalized momentum

$$P_i = \frac{\partial L_V^O}{\partial \dot{\zeta}_i} = \dot{\zeta}_i \quad . \quad (7-51)$$

Hence, the Hamiltonian in the diagonal representation is

$$H_V^O = T_V^O + V_V^O = \frac{1}{2} \sum_i \left(P_i^2 + \omega_i^2 \zeta_i^2 \right) . \quad (7-52)$$

Because the preceding Hamiltonian is in a diagonal representation, we can construct the Hamiltonian operator needed in Eq. (7-10):

$$\hat{H}_V^O = \frac{1}{2} \sum_i \left(\hat{P}_i^2 + \omega_i^2 \hat{\zeta}_i^2 \right) . \quad (7-53)$$

The preceding operator is the Hamiltonian operator for a collection of independent harmonic oscillators. Each frequency, ω_i , is the frequency of vibration of a normal mode. Because the eigenenergies of each mode are independent we can write the eigenvector as a direct product of harmonic oscillator states, i.e.,

$$| i(V)\alpha \rangle = | v_1, v_2, \dots, v_D \rangle_\alpha \quad , \quad (7-54)$$

where v_i is the quantum number for the i^{th} mode. To obtain a Schrödinger wave equation for the purpose of finding the eigenenergies, we combine Eqs. (7-10), (7-53), and (7-54); operate on the result with the position bra $\langle \zeta_1, \zeta_2, \dots, \zeta_i, \dots, \zeta_D |$; and use the theorem of Eq. (2-64) and Eq. (2-66) to obtain

$$\frac{1}{2} \sum_i \left(-\hbar^2 \frac{\partial^2}{\partial \zeta_i^2} + \omega_i^2 \zeta_i^2 \right) \prod_i \psi_v(\zeta_i) = \epsilon_{v\alpha}^0 \prod_i \psi_v(\zeta_i) \quad , \quad (7-55)$$

This equation has the well-known solution:

$$\epsilon_{v\alpha}^0 = \sum_{i=1}^{D(\alpha)} \hbar \omega_i (v + 1/2) \quad . \quad (7-56)$$

The eigenenergy, $\epsilon_{v\alpha}^0$, represents the energy levels of a group of harmonic oscillators that are connected by a phase factor. We can make an anharmonic correction by adding a perturbation term to the Hamiltonian of Eq. (7-52), i.e., the complete vibration Hamiltonian is

$$H_V = H_V^0 + H_V^1 \quad , \quad (7-57)$$

where H_V^1 is a perturbation term. The perturbation is a correction to the potential-energy term that can be written as a further expansion in the normal mode coordinates ζ_i , i.e.,

$$H_V^1 = \sum_i \left(b_i \zeta_i^3 + c_i \zeta_i^4 \right) \quad . \quad (7-58)$$

The perturbation term of the Hamiltonian will add a term to the eigenenergy of Eq. (7-56), see for example Dicke and Wittke (1960, Ch. 14); hence, the eigenenergy of vibration is

$$\epsilon_{\nu\alpha} = \epsilon_{\nu\alpha}^0 + \epsilon_{\nu\alpha}^1 \quad . \quad (7-59)$$

By substituting Eq. (7-59) into Eq. (7-15), using the condition $\epsilon_{\nu\alpha}^1 \ll \epsilon_{\nu\alpha}^0$, using the series expansion for the exponential of $\epsilon_{\nu\alpha}^1$, and using Eq. (6-54); we find that the vibrational partition function is approximately the product of two factors:

$$Q_{\alpha}^V \approx Q_{\alpha}^{V0} Q_{\alpha}^{V1} = Q_{\alpha}^{V1} \sum_{\nu} e^{-\epsilon_{\nu\alpha}^0/kT} \quad . \quad (7-60)$$

We are summing over states; hence, a unit degeneracy factor is used in the preceding equation. From Eqs. (7-18) and (7-60) the free energy of vibration is the sum of two terms

$$F_{\alpha}^V = F_{\alpha}^{V0} + \tilde{F}_{\alpha}^{V1} \quad , \quad (7-61)$$

where

$$F_{\alpha}^{V0} = - kT \ln Q_{\alpha}^{V0} \quad (7-62)$$

and

$$\tilde{F}_{\alpha}^{V1} = - kT \ln Q_{\alpha}^{V1} \quad . \quad (7-63)$$

The harmonic oscillator eigenenergy from Eq. (7-56) can be substituted into Eq. (7-60) to construct the vibrational partition function for a cluster of α molecules:

$$Q_{\alpha}^{Vo} = \prod_{i=1}^{D(\alpha)} \sum_{v=0}^{\infty} e^{-\hbar \omega_i (v + 1/2)/kT} \quad (7-64)$$

The sum over quantum numbers can be completed and then the Helmholtz free energy of vibration can be computed from Eq. (7-62)

$$F_{\alpha}^{Vo} = \frac{\hbar}{2} \sum_{i=1}^{D(\alpha)} \omega_i + kT \sum_{i=1}^{D(\alpha)} \ln \left(1 - e^{-\hbar \omega_i / kT} \right) \quad (7-65)$$

The first term represents the zero-temperature energy, i.e., the difference in energy at $T = 0$ K and the bottom of a potential well. The location of the bottom of the well is determined by W_{α} in Eq. (7-16). If we define a temperature-dependent Helmholtz free energy of vibration for energy levels above the ground state (zero-temperature energy) as

$$\tilde{F}_{\alpha}^{Vo}(T) = kT \sum_{i=1}^{D(\alpha)} \ln \left(1 - e^{-\hbar \omega_i / kT} \right) \quad (7-66)$$

we may combine Eqs. (7-19) for F_{α}^I , (7-61) for F_{α}^V , and (7-66) for $\tilde{F}_{\alpha}^{Vo}$ to obtain an internal Helmholtz free energy:

$$F_{\alpha}^I(T) = -W_{\alpha} + \frac{\hbar}{2} \sum_{i=1}^{D(\alpha)} \omega_i + F_{\alpha}^R(T) + \tilde{F}_{\alpha}^{Vo}(T) + \tilde{F}_{\alpha}^{Vl}(T) \quad (7-67)$$

The first two terms on the right-hand side of Eq. (7-67) combine into a single term

$$U_{\alpha} \equiv W_{\alpha} - \frac{\hbar}{2} \sum_{i=1}^{D(\alpha)} \omega_i \quad (7-68)$$

The quantity U_α is the zero-temperature separation energy, i.e., the binding energy of the cluster. To establish an energy reference point we choose the binding energy of the monomer to be zero, i.e., $U_1 = 0$. After combining Eqs. (7-67) and (7-68) the internal Helmholtz free energy is

$$F_\alpha^I = -U_\alpha + F_\alpha^R + \tilde{F}_\alpha^V, \quad (7-69)$$

where

$$\tilde{F}_\alpha^V \equiv \tilde{F}_\alpha^{V0} + \tilde{F}_\alpha^{V1}. \quad (7-70)$$

We have approximated the internal potential for vibrational modes of each particle in a cluster by a harmonic oscillator potential [see Eqs. (7-44) and (7-49)]; hence, the binding energy U_α cannot be determined from the potential function and we will have to introduce an alternative method later in the development. The relative relationship of the average binding energy $u_\alpha = U_\alpha/\alpha$, W_α/α , and the energy levels of a set of harmonic oscillators is shown in Fig. 5.

To evaluate $\tilde{F}_\alpha^{V0}$ from Eq. (7-66), we convert the sum to an integral, i.e., let

$$\sum_{i=1}^D \longrightarrow \int_0^D di. \quad (7-71)$$

Assuming that there is an inverse function $i(\omega)$ corresponding to ω_i , we can make a change of variables for integration, i.e., let

$$\mathcal{V}(\omega) = \frac{di(\omega)}{d\omega} \quad (7-72)$$

Figure 3

Schematic of harmonic oscillator potentials as a function of position in one plane of a cluster to show location of potential-well minima, relative energy levels, and zero-temperature energy.

be the density of states (the number of degrees of freedom per vibrational mode). Then Eq. (7-66) becomes

$$\tilde{F}_{\alpha}^{Vo}(T) = kT \int_{\omega_0}^{\omega_D(\alpha)} d\omega \mathcal{D}_{\alpha}(\omega) \ln \left(1 - e^{-\hbar\omega/kT} \right) . \quad (7-73)$$

In addition to the previous equation there is another equation containing $\mathcal{D}_{\alpha}(\omega)$. Upon integration of Eq. (7-71) and equating the result to the same integral with a change of variables given by Eq. (7-72):

$$\int_{\omega_0}^{\omega_D(\alpha)} d\omega \mathcal{D}_{\alpha}(\omega) = D(\alpha) . \quad (7-74)$$

The normal modes of vibration will all be coupled together to produce cluster vibrations; hence, boundary conditions imposed by the finite size of clusters are expected to determine the density of states. The total cluster motion can be determined by a classical analysis. Displacements in the generalized coordinate system are given as a function of displacements in the normal-mode coordinate system by the transformation equation, Eq. (7-47). The displacements in the normal-modes coordinates are easily obtained from the Hamiltonian, Eq. (7-52), by solving Hamiltonian's equations of motion:

$$\dot{\zeta}_i = \frac{\partial H_V^0}{\partial p_i} , \quad \dot{p}_i = - \frac{\partial H_V^0}{\partial \zeta_i} . \quad (7-75)$$

The result is

$$\zeta_i = C_i e^{-i \omega_i t} + C_i^* e^{i \omega_i t} . \quad (7-76)$$

The constants of integration are chosen to make ζ_i real. Substituting ζ_i from Eq. (7-76) into the transformation equation Eq. (7-47) produces

$$\eta_i(t) = \sum_j a_{ij} \left(C_j e^{-i\omega_j t} + C_j^* e^{i\omega_j t} \right) . \quad (7-77)$$

Instead of writing the displacement as a function of molecule and coordinate designated by the subscript i , we can write displacement as a continuous function of position:

$$\eta_i(t) \longrightarrow \eta(\vec{r}, t) , \quad (7-78)$$

and similarly,

$$a_{ij} \longrightarrow a_j(\vec{r}) . \quad (7-79)$$

By using Eqs. (7-78) and (7-79), the displacement [from Eq. (7-77)] becomes

$$\eta(\vec{r}, t) = \sum_j a_j(\vec{r}) \left(C_j e^{-i\omega_j t} + C_j^* e^{i\omega_j t} \right) . \quad (7-80)$$

Goldstein (1950, Ch. 11) derives a wave equation for the displacement. The method involves evaluation of T_V from Eq. (7-43) and V_V from Eq. (7-44) in a Cartesian coordinate system and using Lagrange's equation to obtain a second-order differential equation:

$$\frac{\partial^2 \eta(\vec{r}, t)}{\partial t^2} - c^2 \nabla^2 \eta(\vec{r}, t) = 0 , \quad (7-81)$$

where $\bar{c}$ is the average sound velocity. The continuous transformation function can be found by combining Eqs. (7-80) and (7-81). After solving the second-order differential equation and imposing the periodic boundary condition [i.e., that $\eta(\vec{r}, \cdot) = 0$ at the edges of the cluster with dimensions a , b , and c]:

$$a_j(\vec{r}) = \text{const} \sin(k_{xj}X) \sin(k_{yj}Y) \sin(k_{zj}Z) , \quad (7-82)$$

where we have specified the identity

$$\omega_j \equiv \bar{c} \left(k_{xj}^2 + k_{yj}^2 + k_{zj}^2 \right)^{1/2} . \quad (7-83)$$

The solution for the displacement given by Eq. (7-80) is a solution of the wave equation Eq. (7-81) in terms of a Fourier series expansion that has fundamental frequencies given by frequencies of the normal-mode vibrations. The transformation function $a_j(\vec{r})$ introduces the phase factor that allows the normal modes of vibration to produce wave motion.

It can be seen from Eq. (7-83) that each value of $\omega_j/\bar{c}$ represents the length of a vector in k -space. The boundary conditions yield the vector components in k -space:

$$k_{xj} = \frac{2\pi}{a} \ell , \quad k_{yj} = \frac{2\pi}{b} m , \quad k_{zj} = \frac{2\pi}{c} n , \quad (7-84)$$

where ℓ , m , n are integers. A volume in k -space is

$$k_{xj} k_{yj} k_{zj} = \frac{(2\pi)^3}{V} \ell m n , \quad (7-85)$$

where $V = abc$ is the volume of the cluster. Each integer given by the product lmn , represents an allowed mode of natural vibration (a value of ω_j) in k -space, i.e., a different value of j . Hence;

$$\frac{d\vec{k}_j}{dj} = \frac{(2\pi)^3}{V} , \quad (7-86)$$

where $d\vec{k}_j$ is an element of volume in k -space. Changing to spherical coordinates in k -space,

$$d\vec{k}_j = 4\pi k_j^2 dk_j , \quad (7-87)$$

and the dispersion relation from Eq. (7-83) yields

$$dj = \frac{V}{2\pi^2} \frac{\omega^2}{c^3} d\omega . \quad (7-88)$$

From Eqs. (7-72) and (7-88) we obtain the usual density of states [see for example, Kittel (1971, p. 212) or Zharkov and Kalinin (1971, p. 22)]:

$$\mathcal{D}(\omega) = \xi \frac{V}{2\pi^2} \frac{\omega^2}{c^3} . \quad (7-89)$$

The factor ξ has been inserted on the right-hand side to account for multiple polarization, i.e., $\eta(\vec{r}, t)$ is a displacement in one direction and the process leading to $\mathcal{D}(\omega)$ with $\xi = 1$ can be repeated for the other components of the displacement. For crystals $\xi = 3$ (two transverse displacements and one longitudinal); however, for liquids $\xi = 1$ because liquids have no shear strength.

The upper limit of integration in terms of the number of degrees of freedom in the cluster can be determined by substituting Eq. (7-89) into Eq. (7-74). The result is:

$$\omega_D = \left[\frac{6 \pi^2 D(\alpha)}{\xi V_\alpha} \right]^{1/3} \bar{c} . \quad (7-90)$$

The frequency is known as the Debye frequency. A more frequently used quantity is the Debye temperature

$$\Theta = \frac{\hbar \omega_D}{k} . \quad (7-91)$$

To obtain the vibration free energy as a function of the Debye temperature, we can substitute Eq. (7-89) into Eq. (7-73) and use Eq. (7-91) to obtain the standard result:

$$\tilde{F}_\alpha^{Vo} = 3 D(\alpha) \left(\frac{T}{\Theta} \right)^3 kT \int_0^{\Theta/T} dx x^2 \ln (1 - e^{-x}) . \quad (7-92)$$

The Bose functions described in App. I provide a convenient method for evaluating the integrals in Eq. (7-92). In terms of Bose functions the Helmholtz free energy of harmonic vibration in a cluster of α molecules is

$$\begin{aligned} \tilde{F}_\alpha^{Vo}(T, \Theta) = & - 3 D(\alpha) \left(\frac{T}{\Theta} \right)^3 kT \left\{ 2 \left[g_4(1) - g_4(e^{-\Theta/T}) \right] \right. \\ & \left. - 2 \left(\frac{\Theta}{T} \right) g_3(e^{-\Theta/T}) - \left(\frac{\Theta}{T} \right)^2 g_2(e^{-\Theta/T}) \right\} . \end{aligned} \quad (7-93)$$

At high temperature ($\Theta/T < 1$) the harmonic oscillator vibrational free energy represented by Eq. (7-92) approaches the classical result,

$$\tilde{F}_\alpha^{Vo} \approx D(\alpha) kT \ln \left(\frac{\Theta}{T} \right) , \quad (7-94)$$

where $\Theta = \hbar \bar{\omega} / k$ and $\bar{\omega}$ is an average angular frequency of vibration. The anharmonic correction term to the free energy F_{α}^{V1} is expected to be noticeable only at high temperature [see Zharkov and Kalinin (1971, p. 32)]; hence, the perturbation free energy from a classical analysis derived by Zharkov and Kalinin (1971) is applicable. The Hamiltonian for evaluating the classical partition function, from Eqs. (7-57), (7-52), and (7-58), is:

$$H_V = \sum_i \left\{ \frac{1}{2} (p_i^2 + \omega_i^2 \zeta_i^2) + b_i \zeta_i^3 + c_i \zeta_i^4 \right\} . \quad (7-95)$$

Evaluation of the classical partition function,

$$Q_{\alpha}^V(i) = \frac{1}{h} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dP_i d\zeta_i e^{-H(P_i, \zeta_i)/kT} , \quad (7-96)$$

with H_V from Eq. (7-95) yields for a single degree of freedom:

$$\tilde{F}_{\alpha}^V(i) = -kT \ln \left(\frac{\hbar \omega_i}{kT} \right) - kT \ln \left[1 - \frac{1}{\omega_i^4} \left\{ 3 c_i - 15 \left(\frac{b_i}{\omega_i} \right)^2 \right\} kT \right] , \quad (7-97)$$

as derived by Zharkov and Kalinin (1971). From Eqs. (7-97), (7-94), and (7-61) we conclude that for $A_{\alpha} \ll kT$, the perturbation free energy is

$$\tilde{F}_{\alpha}^{V1} \approx -D(\alpha) A_{\alpha} (kT)^2 , \quad (7-98)$$

where A_{α} is an average value of $-[3c_i - 15(b_i/\omega_i)^2]/\omega_i^4$. Note that the sign of A_{α} cannot be determined in advance.

The internal Helmholtz free energies can be used to find the internal energy of each cluster. Application of Eq. (6-54) to Eq. (7-69), yields:

$$E_{\alpha}^I = -U_{\alpha} + E_{\alpha}^R(T) + \tilde{E}_{\alpha}^{Vo}(T, \Theta) + \tilde{E}_{\alpha}^{V1}(T) \quad , \quad (7-99)$$

where

$$E_{\alpha}^R(T) = \frac{3}{2} kT \quad , \quad (7-100)$$

$$\begin{aligned} \tilde{E}_{\alpha}^{Vo}(T, \Theta) = & 3 D(\alpha) \left(\frac{T}{\Theta} \right)^3 kT \left\{ 6 \left[g_4(1) - g_4(e^{-\Theta/T}) \right] \right. \\ & \left. - 6 \left(\frac{\Theta}{T} \right) g_3(e^{-\Theta/T}) - 3 \left(\frac{\Theta}{T} \right)^2 g_2(e^{-\Theta/T}) - \left(\frac{\Theta}{T} \right)^3 g_1(e^{-\Theta/T}) \right\} \quad , \quad (7-101) \end{aligned}$$

and

$$\tilde{E}_{\alpha}^{V1}(T) = D(\alpha) A_{\alpha} (kT)^2 \quad . \quad (7-102)$$

In the preceding derivation of the vibrational free energy, it is implied that the Debye temperature Θ for each cluster size is different; see Eq. (7-90). The Debye temperature depends on the number of degrees of freedom per molecule (especially for small clusters) and on the sound velocity, $\bar{c}$, which is a function of the compressibility and; hence, of the potential or binding energy of the cluster. In a more basic sense the functional dependence of Θ on binding energy is a consequence of cluster vibrations being superpositions of normal mode vibration, which, in turn, depend on the binding energy of each molecule in the cluster.

With respect to binding potential energy, a cluster can be considered to be composed of two types of molecules: (1) "interior molecules" that are completely surrounded by other molecules and; hence, are bound in a potential well very similar to molecules in the infinite medium, and (2) "surface molecules" that are bound in a more shallow potential well because there are fewer molecules for such a molecule to form bonds with. Because the molecules in a cluster can be classified into two types according to their binding potential, we propose: cluster vibrations can be described by two Debye temperatures, Θ_i for interior molecules and Θ_s for surface molecules, as an alternative to having a Debye temperature for every cluster size. Similarly, interior and surface molecules are expected to have different anharmonic correction coefficients. Let n_α^i be the number of interior molecules in a cluster of α molecules and n_α^s be the number of surface molecules in the same cluster. Then molecule conservation requires,

$$n_\alpha^i + n_\alpha^s = \alpha \quad . \quad (7-103)$$

In addition to allowing interior and surface molecules to have different Debye temperatures, it is consistent to assign a different zero-point energy to each class of molecules. From the preceding considerations, Eq. (7-67) for the interior Helmholtz free energy can be written

$$\begin{aligned} F_\alpha^I(T) = & F_\alpha^R(T) + \frac{n_\alpha^i}{\alpha} \left[\tilde{F}_\alpha^{Vo}(T, \Theta_i) - U_\alpha^i - D(\alpha) A^i (kT)^2 \right] \\ & + \frac{n_\alpha^s}{\alpha} \left[\tilde{F}_\alpha^{Vo}(T, \Theta_s) - U_\alpha^s - D(\alpha) A^s (kT)^2 \right] \quad . \end{aligned} \quad (7-104)$$

The number of degrees of freedom in a cluster of α molecules can be written as a product of factors:

$$D(\alpha) = 3 \alpha \chi(\alpha) \kappa \quad (7-105)$$

The factor 3 denotes the number of dimensions per particle, $\chi(\alpha)$ is a factor that accounts for degrees of freedom assigned to rotation and translation of small clusters, and κ is a number that can vary from one to the number of atoms per molecule. If all the atoms of a molecule move as a unit, $\kappa = 1$; and if each atom is considered a particle, κ is the number of atoms per molecule. The factor $\chi(\alpha)$ approaches a limiting value of unity when α is large. In an infinite medium the vibrational free energy per molecule is

$$\begin{aligned} \tilde{f}_{\infty}^V(T, \Theta, A) &= \tilde{f}_{\infty}^{Vo}(T, \Theta) + f_{\infty}^{V1}(T, A) \\ &= 9 \kappa \left(\frac{T}{\Theta} \right)^3 kT \left\{ 2 \left[g_4(1) - g_4(e^{-\Theta/T}) \right] \right. \\ &\quad \left. - 2 \left(\frac{\Theta}{T} \right) g_3(e^{-\Theta/T}) - \left(\frac{\Theta}{T} \right)^2 g_2(e^{-\Theta/T}) \right\} - 3 \kappa A (kT)^2 \quad (7-106) \end{aligned}$$

For a Debye temperature Θ and an anharmonic correction factor A , which are independent of cluster size, the vibrational free energy per molecule [from Eq. (7-70) for $\tilde{F}_{\alpha}^V$, Eq. (7-93) for $\tilde{F}_{\alpha}^{Vo}$, Eq. (7-98) for $\tilde{F}_{\alpha}^{V1}$, Eq. (7-105) for $D(\alpha)$, and Eq. (7-106) for $\tilde{f}_{\alpha}^V$] is:

$$\tilde{f}_{\alpha}^V(T, \Theta, A) \equiv \frac{1}{\alpha} \tilde{F}_{\alpha}^V(T, \Theta, A) = \chi(\alpha) \tilde{f}_{\infty}^V(T, \Theta, A) \quad (7-107)$$

The binding energy per molecule is defined by

$$u_{\alpha} \equiv \frac{1}{\alpha} U_{\alpha} \quad (7-108)$$

We substitute Eq. (7-103) for n_{α}^i , Eq. (7-107) for $\tilde{f}_{\alpha}^V$, and Eq. (7-108) for u_{α} into Eq. (7-104) to obtain the internal Helmholtz free energy in the following form:

$$\begin{aligned} F_{\alpha}^I(T) = & F_{\alpha}^R(T) + n_{\alpha}^{\delta} \left[u_{\alpha}^i - u_{\alpha}^{\delta} + \chi(\alpha) \tilde{f}_{\infty}^V(T, \Theta_{\delta}, A^{\delta}) \right. \\ & \left. - \tilde{f}_{\infty}^V(T, \Theta_1, A^i) \right] + \alpha \left[\tilde{f}_{\infty}^V(T, \Theta_j, A^i) - u_{\infty}^i \right] \quad (7-109) \end{aligned}$$

If a cluster contains only a few molecules they will all be surface molecules; hence, in deriving Eq. (7-109) we set $\chi(\alpha) = 1$ when Eq. (7-107) is applied to interior molecules. For infinite-size clusters the rotational term and surface term are negligible; hence, the last term in Eq. (7-109) is the internal free energy per molecule for a molecule in an infinite medium, i.e.,

$$f_{\infty}^I(T) = f_{\infty}^i(T) = \tilde{f}_{\infty}^V(T, \Theta_1, A_1^i) - u_{\infty}^i \quad (7-110)$$

The Helmholtz free-energy difference required to calculate the saturation volume and pressure by Eqs. (6-79) and (6-80) is found by combining Eqs. (7-109) and (7-110):

$$\begin{aligned} F_{\alpha}^I(T) - \alpha f_{\alpha}^I(T) = & F_{\alpha}^R(T) \\ & + n_{\alpha}^{\delta} \left[u_{\infty}^i - u_{\alpha}^{\delta} + \chi(\alpha) \tilde{f}_{\infty}^V(T, \Theta_{\delta}, A^{\delta}) - \tilde{f}_{\infty}^V(T, \Theta_1, A^i) \right] \quad (7-111) \end{aligned}$$

for an equilibrium state and $\mu = \mu_1$, the chemical potential equals the internal free energy, i.e., $\mu = f_1^i(T)$; hence, the free energy difference given by Eq. (7-111) is necessary for calculating the equilibrium distribution from Eq. (6-58) and consequently the droplet current from Eq. (5-58).

In small clusters ($\alpha \lesssim 40$), all molecules will be surface molecules, i.e., the number of surface molecules will be

$$n_{\alpha}^{\delta} = \alpha \quad . \quad (7-112)$$

For large clusters, a uniform surface density of σ molecules per unit area is established, and a surface area can be computed from macroscopic properties. If we define a unit radius as

$$R_1(T) = \left(\frac{3 \cdot m}{4\pi \cdot \rho(T)} \right)^{1/3} , \quad (7-113)$$

the radius of a large cluster is

$$R_{\alpha}(T) = R_1(T) \cdot \alpha^{1/3} . \quad (7-114)$$

The cluster radius is a function of temperature because the density can vary with temperature. Hence, for large clusters the number of surface molecules is

$$n_{\alpha}^{\delta} = 4\pi R_1(T)^2 \cdot \sigma(T) \cdot \alpha^{2/3} . \quad (7-115)$$

The two equations for n_{α}^{δ} , Eq. (7-112) and Eq. (7-115), yield the same n_{α}^{δ} at

$$\alpha_c = \left[4\pi R_1(T)^2 c(T) \right]^{3/5} \quad (7-116)$$

The first equation for n_α^δ , Eq. (7-112), overestimates the number of surface molecules when $\alpha > \alpha_c$, and the second equation, Eq. (7-115), overestimates n_α^δ when $\alpha < \alpha_c$; hence, the two equations can be combined into a single equation for n_α^δ by using the minimum of the two computed values, i.e.,

$$n_\alpha^\delta = \min (\alpha, 4\pi R_1^2 c \alpha^{2/3}) \quad (7-117)$$

The result has a discontinuous derivative at $\alpha = \alpha_c$ and this can cause a problem when calculating the droplet current; see Eq. (5-70). A function that approximates Eq. (7-117) and has continuous derivatives can be found by noting that the two parts of Eq. (7-117) are straight lines on a plot of $\ln n_\alpha^\delta$ versus $\ln \alpha$. By making these straight lines the asymptotes of a hyperbola, we obtain the following equation for the number of surface molecules:

$$n_\alpha^\delta = \alpha_c e^{\left[0.8333 \ln \left(\frac{\alpha}{\alpha_c} \right) - \sqrt{0.027778 \left(\ln \frac{\alpha}{\alpha_c} \right)^2 + 1.6832 \delta^2} \right]} \quad (7-118)$$

The distance between the crossing point of the asymptotes of the hyperbola and the intercept of the hyperbola with the bisector of the asymptotes (on a log-log plot of n_α^δ versus α) is δ , a free parameter. As δ approaches zero, the curve represented by Eq. (7-118) approaches the curve represented by Eq. (7-17). We have used $\delta = 0.001$ in our numerical work.

For small clusters [where Eq. (7-111) is applicable], u_{α}^{δ} is the total binding energy per molecule for a cluster of α molecules. Some calculations of binding energies by the Hartree-Fock method have been reported for small water clusters by Kistenmacher et al (1974); however, the required data are generally not available. In lieu of available data one may use a phenomenological formula suggested by Freund and Bauer (1977). An adaptation of their equation to surface molecules is

$$u_{\alpha}^{\delta} = u_{\infty}^{\delta} (1 - \alpha^{-p}) \quad , \quad (7-119)$$

where u_{α}^{δ} and p are parameters to be determined. This function has a steep rise at small α , as it must, according to Kistenmacher et al (1974) calculations, and asymptotically approaches a maximum value u_{∞}^{δ} , which is the binding energy of a molecule on the surface of a macroscopic piece of material.

For large clusters, the free-energy difference of Eq. (7-111) reduces to

$$F_{\alpha}^I(T) - \alpha f_{\infty}^I(T) = 4\pi R_1^2 \sigma \alpha^{2/3} \\ \left\{ u_{\infty}^i - u_{\infty}^{\delta} + \tilde{f}_{\infty}^V(T, \Theta_{\delta}, A^{\delta}) - \tilde{f}_{\infty}^V(T, \Theta_i, A^i) \right\} \quad . \quad (7-120)$$

If we define

$$f_{\infty}^{\delta}(T) = \tilde{f}_{\infty}^V(T, \Theta_{\delta}, A^{\delta}) - u_{\infty}^{\delta} \quad (7-121)$$

as the Helmholtz free energy of a molecule on the surface of a condensed material and use Eqs. (7-110), Eqs. (7-120) and (7-121) combine for a Helmholtz free-energy difference:

$$F_1^I(T) - \alpha f_\infty^I(T) = 4\pi R_\alpha(T)^2 c(T) \left(f_\infty^S(T) - f_\infty^I(T) \right) . \quad (7-122)$$

Hirschfelder, Curtis, and Bird (1954, p. 341) have shown that (if the surface is flat) the surface tension is the change in Helmholtz free energy per unit area required to move the surface molecules from the interior of a liquid to the surface; i.e., in our notation the surface tension is

$$\gamma(T) = c(T) \left(f_\infty^S(T) - f_\infty^I(T) \right) . \quad (7-123)$$

By combining Eqs. (7-122) and (7-123) we have

$$F_\alpha^I(T) - \alpha f_\infty^I(T) = 4\pi R_\alpha(T)^2 \gamma(T) . \quad (7-124)$$

The surface tension is the energy per unit area required to increase the area of a thin film. It has cgs units of dyne/cm; therefore, it can also be thought of as the force per unit length of film edge required to maintain the film in a stretched position. The surface tension is not a restoring force; i.e., it does not depend on the amount of stretch a film has been given. As the film is stretched, work is done because the molecules are moved from the interior to the surface. The result, Eq. (7-124), that we have derived (by allowing surface molecules to have different binding energies and Debye temperatures than interior molecules)

is a fundamental assumption in classical nucleation theory. See for example, McDonald (1962). Because Eq. (7-124) is a large-cluster-limiting case of Eq. (7-111) it cannot be expected to be very accurate for nucleation at large supersaturation ratios where the free energies of small clusters are important.

The free-energy difference required for nucleation-rate calculations is given by Eq. (7-111). It contains several parameters that are difficult to calculate ab initio, i.e., the Debye temperatures, Θ_g and Θ_l , the infinite-medium binding energy u_{∞}^i , the parameters u_{∞}^s and p for surface-molecule binding energies, and the anharmonic constant A . One of the parameters can be determined if the others are known by using surface tension data and Eq. (7-123). The free-energy difference given by Eq. (7-111) is also required to calculate saturation-line volume and pressure from Eqs. (6-79) and (6-80). Because saturation-line data can be measured accurately, the infinite medium-binding energies and Debye temperatures can be varied to fit the saturation-line data, and the parameters can then be used to calculate nucleation rates in diffusion cloud chamber experiments as a test of the droplet formation theory.

This concludes our development of the Helmholtz free energy of clusters. It includes the free energies of translation, rotation, and vibration. The terms representing vibration occur because molecules move about in a potential well when they are trapped in a cluster. We have included the most easily excited energy modes. Other contributions to the Helmholtz free energy could come from internal molecular vibrational states of the molecules; however, the temperatures are too low in most nucleation experiments to excite these energy levels, and their effects would tend to cancel out because our results depend on free-energy differences.

CHAPTER 8

KINETIC COEFFICIENTS

When we solved the master equation in Ch. 5 we assumed that the kinetic coefficients, A_{α} and B_{α} , could be calculated. In Ch. 6, we noted that the calculation of these coefficients is greatly simplified for temperatures not close to absolute zero. In this chapter, the last chapter on the theoretical development, we will develop equations for growth rate rate by monomer accretion, A_{α} , to the point where this rate can be evaluated approximately for calculations of nucleation rates.

The kinetic coefficient for cluster growth is given by Eq. (4-57). We can use Eq. (2-58) for $\omega_{i\alpha}$, factor M^{-1} out of the delta function, and make the approximation suggested by Eq. (6-44) to rewrite the kinetic coefficient for cluster growth as

$$A_{\alpha,\beta} = h \sum_{ijk} \delta(\epsilon_{i(\alpha+\beta)} - \epsilon_{j\alpha} - \epsilon_{k\beta}) \left| \omega_{i(\alpha+\beta)j\alpha k\beta} \right|^2 \rho_{j\alpha} \rho_{k\beta} . \quad (8-1)$$

The corresponding kinetic coefficient for evaporation is

$$B_{\alpha+\beta,\beta} = h \sum_{ijk} \delta(\epsilon_{i(\alpha+\beta)} - \epsilon_{j\alpha} - \epsilon_{k\beta}) \left| \omega_{i(\alpha+\beta)j\alpha k\beta} \right|^2 \rho_{i(\alpha+\beta)} . \quad (8-2)$$

The expansion coefficient, $\omega_{i(\alpha+\beta)j\alpha k\beta}$, can be written in terms of the interaction operator by taking the scalar product of Eq. (4-2) with single-particle states. After using the properties of single-particle creation and annihilation operators from Eqs. (2-32) through (2-33) and treating $b_{k\gamma}$ from Eq. (4-2) as a single-particle state operator the scalar product yields

$$N^{-1} \rho_{i(\alpha+\beta)j\alpha k\beta} = \langle i(\alpha+\beta) | \hat{V}^{(1)} | j\alpha, k\beta \rangle. \quad (8-3)$$

Combining Eqs. (8-1) and (8-3) yields:

$$A_{\alpha,\beta} = \frac{2\pi}{N} \sum_{ijk} \delta(\epsilon_{i(\alpha+\beta)} - \epsilon_{j\alpha} - \epsilon_{k\beta}) \\ |\langle i(\alpha+\beta) | \hat{V}^{(1)} | j\alpha, k\beta \rangle|^2 \rho_{j\alpha} \rho_{k\beta}. \quad (8-4)$$

For monomer growth, we have, from Eqs. (5-38) and (8-4),

$$A_{\alpha} = \frac{2\pi}{N} \sum_{ijk} \delta(\epsilon_{i(\alpha+1)} - \epsilon_{j\alpha} - \epsilon_{kl}) \\ |\langle i(\alpha+1) | \hat{V}^{(1)} | j\alpha, kl \rangle|^2 \rho_{j\alpha} \rho_{kl}. \quad (8-5)$$

In quantum mechanics a state-to-state cross section is usually defined [see Bond, Watson and Welsh (1965, p. 122)] by

$$N \sigma(i \rightarrow j) v_{\text{rel}} = V w(i \rightarrow j), \quad (8-6)$$

where $w(i \rightarrow j)$ is the transition probability, N/V is the number density of incident particles, $\sigma(i \rightarrow j)$ is the cross section, and v_{rel} is the relative velocity between particles. The transition probability is defined by Eq. (8-5); hence, the state-to-state cross section per molecule is

$$\sigma_{i(\alpha+1)jakl} \equiv \frac{2\pi}{h} \frac{V}{v_{jakl}} \delta(\epsilon_{i(\alpha+1)} - \epsilon_{ja} - \epsilon_{kl})$$

$$= \langle \sigma_{i(\alpha+1)} \rangle \langle V^{(1)} \rangle_{jakl}^2 \quad (8-7)$$

In terms of the cross section, the growth rate for clusters of α molecules by monomer accretion is

$$A_\alpha = \frac{1}{V} \sum_{ijk} \sigma_{i(\alpha+1)jakl} v_{jakl} \rho_{ja} \rho_{kl} = \frac{1}{V} \langle \sigma v_{rel} \rangle_\alpha \quad (8-8)$$

The cross section can be written as the product of the geometrical cross section and a sticking coefficient a_o , i.e.,

$$\sigma_{i(\alpha+1)jakl} = a_o \pi (R_\alpha + R_1)^2 \quad (8-9)$$

The sticking coefficient is expected to be 1.0 for large clusters. For evaluation of A_α , we use Eq. (7-114) for R_α in Eq. (8-9) and substitute the result into Eq. (8-8):

$$A_\alpha = \frac{a_o}{V} \pi R_1^2 (1 + \alpha^{1/3})^2 \langle v_{rel} \rangle_\alpha \quad (8-10)$$

The average relative velocity is

$$\langle v_{rel} \rangle_\alpha = \sum_{jk} v_{jakl} \rho_{ja} \rho_{kl} \quad (8-11)$$

The average relative velocity from Eq. (8-11) can be evaluated by using

Eq. (4-55) for the density of states, taking the translation eigenenergies from Eq. (6-23), converting the sum to an integral, and transforming the velocity variables from Cartesian to center-to-mass coordinates [see Present (1958, p. 79)] to obtain the well-known result

$$\langle v_{rel} \rangle_{\alpha} = \bar{v}_1 \left(\frac{\alpha+1}{\alpha} \right)^{1/2}, \quad (8-12)$$

where

$$\bar{v}_1 \equiv \left(\frac{8}{\pi} \frac{kT}{m} \right)^{1/2}. \quad (8-13)$$

The kinetic coefficient obtained by combining Eqs. (8-10), (8-12), and (8-13) is

$$A_{\alpha} = \frac{a_0}{V} \pi R_1^2 \bar{v}_1 \alpha^{2/3} (1 + 2 \alpha^{-1/3} + \dots) \quad (8-14)$$

The preceding equation for A_{α} and Eq. (5-44), which relates B_{α} to $A_{\alpha-1}$, provide the necessary kinetic coefficients for evaluation of nucleation rates from Eq. (5-58) or Eq. (5-70).

CHAPTER 9

COEXISTENCE LINE OF WATER

Although the nucleation theory that we have developed is general, its successful application to a particular substance will depend on the availability of thermodynamic and structural data for that substance. The techniques for obtaining needed constants from available data will vary with the type of material and with the amount of data available. We shall apply the theory to a particular substance (water) to demonstrate one technique that can be used.

In Ch. 6 we developed Eq. (6-82) for the cluster fraction N_s/N along the coexistence line. This equation is a function of the Helmholtz free energy of all cluster sizes, including the infinite medium. The cluster fraction is also the thermodynamic potential, PV [see Eq. (6-81)], from which the complete equation of state for the two-phase region can be obtained; hence, a set of Helmholtz free energies (for all cluster sizes) that allows matching the PV data via Eq. (6-82) will not only provide a means for obtaining a complete set of equations of state in both the gas phase and the two-phase region, but will also provide required data for computing nucleation rates, see Eq. (5-58). In this chapter we will obtain a set of parameters yielding coexistence-line functions that match experimental data. These parameters will be used in Ch. 10 to calculate nucleation rates in a test of our nucleation theory. We have chosen water because: (1) abundant thermodynamic and coexistence-line data are available, (2) data for both diffusion cloud chamber and nozzle nucleation experiments have been reported, (3) the

structure of small clusters of water molecules has been calculated in detail, and (4) there is practical need for better understanding of nucleation of water in two-phase flow in steam turbines and meteorological studies.

We will first determine the rotational free-energy constants (for clusters of water molecules) from available data. Next, we will employ the high-temperature limit of the Debye free energy and saturation-line data to find the number of degrees of freedom in liquid water. The Debye temperature and the binding energy per molecule of liquid water are determined simultaneously from the vapor pressure curve at temperatures near the triple point where clustering and anharmonic effects are negligible. We will utilize surface-tension data to find the binding energy of a molecule on the surface of an infinite medium and the number of molecules per unit surface area. The remaining parameters, Θ_s , the Debye temperature of a surface molecule, and u_2^δ the binding energy of the dimer, are determined by finding their best fit to cluster-fraction data. The results are then used to calculate saturation pressure, specific volume along the coexistence line, and heats of vaporization for comparison with experiment. Finally, the theoretical and experimental vapor-pressure curve of ice will be matched by varying the binding energy of a molecule in the solid.

From the results of Ch. 7, we can obtain a complete set of rotational temperatures that are directly related to the Helmholtz free energy of rotation by Eq. (7-35). For the water molecule, the symmetry number, σ , in the second term of Eq. (7-35) is unity. For all other clusters, there will be no symmetry; hence, we can drop the symmetry term.

The water molecule (monomer) is an asymmetric rotator; i.e., it has three distinct moments of inertia. Hall and Dowling (1967) present eigenenergies suitable for calculating the rotational partition function from Eq. (7-28). From their data and from Eqs. (7-28) and (7-17) we calculate the rotational free energy as shown in Fig. 4. Hall and Dowling (1967) also present rotational constants for the water molecule: $A = 27.88 \text{ cm}^{-1}$, $B = 14.51 \text{ cm}^{-1}$, and $C = 9.29 \text{ cm}^{-1}$. Substitution of these constants into Eq. (7-34) yields a rotational temperature $T_1^R = 15.28 \text{ K}$. The rotational free energy from Eq. (7-35) with this value of T_1^R is also plotted in Fig. 4. The two methods agree reasonably well; we use the latter for subsequent calculations.

The water dimer is essentially a symmetric top, as evidenced by the rotational constants computed by Braun and Liedecker (1974): $A = 6.653 \text{ cm}^{-1}$, $B = 0.246 \text{ cm}^{-1}$, $C = 0.245 \text{ cm}^{-1}$. Substitution of these constants into Eq. (7-34) yields a rotational temperature, $T_2^R = 0.725 \text{ K}$.

Kistenmacher et al (1974) have studied the binding energy of various configurations of water molecules in small clusters (2 to 8 molecules) by using Hartree-Fock derived potentials to determine the most probable configurations. Their configuration for a trimer locates the water molecules at the points of a triangle that is essentially equilateral. The sides of the triangle are 2.96, 2.96, and 2.97 Å long. We assume that the molecules are point masses located at the points of the triangle and calculate moments of inertia, and subsequently, rotational constants from Eq. (7-31). The result is $A = 0.0819 \text{ cm}^{-1}$ and $B = C = 0.1069 \text{ cm}^{-1}$. From Eq. (7-34) the rotational temperature $T_3^R = 0.0954 \text{ K}$.

Kistenmacher et al (1974) find that the strongest tetramer binding configuration is a square with a molecule at each corner. The distance

Figure 4

Helmholtz free energy of rotation for the water molecule computed from Hall and Dowling (1967) data.

————— From rotational constants
 - - - - - From energy levels

between molecules along the edges of the square is $2.96 \text{ \AA}$. From this configuration we compute the rotational constants $A = 0.05347 \text{ cm}^{-1}$ and $B = C = 0.1069 \text{ cm}^{-1}$, and a rotational temperature $T_4^R = 0.0834 \text{ K}$.

For the pentamer, Kistenmacher et al (1974) find that the most stable configuration is a ring of molecules. The perimeter distance between molecules is $2.96 \text{ \AA}$. For this configuration, $T_5^R = 0.0460 \text{ K}$.

In their studies of clusters of six or more molecules, Kistenmacher et al (1974) found that several configurations give the same binding energy and that the ring structure is not preferential. For clusters of six or more molecules we assume that the configuration is a uniform sphere and calculate the rotational temperature from Eq. (7-39). The rotational temperatures that we use for calculating the rotational contribution to the free energy are summarized in Table 1. We also include spherical-top temperatures for clusters of less than six molecules for comparison with detailed calculations; however, the spherical-top model is not very accurate for very small clusters.

Equation (7-106) for the vibrational free energy of the infinite medium requires evaluation of 3κ , the number of degrees of freedom per molecule, and of Θ_i , the Debye temperature. To find κ , we calculate the internal energy in a high-temperature limit and compare the result with experimental data. Further confirmation is found by comparing calculated entropy and Helmholtz free energy with experimental results. At high temperature, we can replace e^{-x} by $1 - x$ in Eq. (7-92). After substitution, we complete the integration and use Eq. (7-105) for $D(\alpha)$ and the large cluster limit of Eq. (7-107) for $\tilde{F}_\alpha^V$ to obtain the following equation that is an approximation to Eq. (7-106):

Table 1

Summary of rotational temperatures for clusters of water molecules. Spherical-top calculations for $\alpha \leq 5$ are included for comparison with values discussed in text.

<u>Cluster Size, α</u>	<u>Rotation Temperature, T_{α}^R (K)</u>	
	<u>For This Work</u>	<u>Spherical Top Eq. (7-35)</u>
1	15.28	0.6209
2	0.725	0.1956
3	0.0954	0.0995
4	0.0834	0.0616
5	0.0460	0.0425
6		0.0313
7		0.0242
8		0.0194
9		0.0159
10		0.0134

$$\tilde{f}_{\infty}^V(T, \Theta, A) = 3 \kappa kT \left[\ln \left(\frac{\Theta}{T} \right) - \frac{1}{3} - A kT \right] . \quad (9-1)$$

The internal energy above the zero-point energy can be obtained from the preceding results; i.e., application of Eq. (6-54) to Eq. (9-1) yields

$$\tilde{\epsilon}_{\infty}^V(T, \Theta, A) = 3 \kappa kT (1 + A kT) , \quad (9-2)$$

where $\tilde{\epsilon}_{\alpha}^V = \frac{1}{\alpha} \tilde{E}_{\alpha}^V$ and $\epsilon_{\alpha}^V = \tilde{\epsilon}_{\alpha}^V - u_{\alpha}$. Ražnjević (1976) presents tabulated experimental data of pressure, specific volume, density, enthalpy, heat of vaporization, and entropy of water as a function of temperature (along the coexistence line). For the tabulated data both enthalpy and entropy are zero at $T = T_t$, the triple-point temperature; i.e., the tabulated enthalpy is

$$\Delta h = h(T) - h(T_t) \quad (9-3)$$

and the tabulated entropy is

$$\Delta s = s(T) - s(T_t) . \quad (9-4)$$

To find the internal energy, we use the definition

$$\Delta \epsilon = \Delta h - P v , \quad (9-5)$$

where P is the tabulated pressure and v is the tabulated specific volume of the liquid. Note that the Pv term is negligible at $T = T_t$; hence, analytic forms of $\Delta \epsilon$ are computed from

$$\Delta \epsilon = \epsilon_{\infty}^I(T) - \epsilon_{\infty}^I(T_t) \quad . \quad (9-6)$$

An approximate analytic equation for the internal energy difference from Eqs. (9-2) and (9-6) is:

$$\Delta \epsilon = 3 \kappa k(T - T_t) [1 + A k(T + T_t)] \quad . \quad (9-7)$$

Note that the zero-point energies cancel out in the derivation of Eq. (9-7). The internal energy of liquid water from tabulated data of Ražnjević (1976) and Eq. (9-5) are compared to Eq. (9-7) with $\kappa = 3$ (for nine degrees of freedom) and $A = 0$ in Fig. 5. The energy difference from Eq. (9-7) represents a maximum value of a result that could be obtained from a more accurate Debye approximation, Eq. (7-101). Also, the maximum number of degrees of freedom is nine. Because the experimental data are higher and because the curves are nearly identical for $T = 273$ to 500 K, we conclude that there are nine degrees of freedom per molecule in liquid water and that there is a negative anharmonic correction term for the Helmholtz free energy of vibration.

The entropy of vibration per molecule in the infinite medium can be obtained directly from Eqs. (9-1) and (9-2). The Helmholtz free energy $\tilde{f}_{\infty}^V(t, \Theta, A)$ has an associated partition function Q_{∞}^V (a canonical ensemble) that allows evaluation of equations of state for the liquid (or solid) medium. The derivation is presented by Huang (1963, p. 158) for the classical partition function, but it is equally valid for the quantum mechanical partition function. The equation for the entropy is similar to the Euler equation, i.e.,

Figure 5

Internal energy per molecule, $\Delta\epsilon$, of liquid water as a function of temperature.

- Experimental data from Ráznjević (1976) and Eq. (9-5).
- From Eq. (9-7) with $\kappa = 3$ and $A = 0$.
- · - · - From Eqs. (9-6) and (7-101) with $\kappa = 3$ and $\Theta = 435.9$ K and $A = 0$.

$$T \Delta s_{\infty} = \epsilon_{\infty} - f_{\infty} \quad . \quad (9-8)$$

A binding energy can be added to Eqs. (9-1) and (9-2) to obtain absolute free energy and internal energy [see Eq. (7-12)]; however, the binding energies cancel when the results are substituted into Eq. (9-8) and we obtain

$$\Delta s_{\infty} = 3 \kappa k \left[\frac{4}{3} - \ln \left(\frac{\Theta}{T} \right) + 2 A k T \right] \quad (9-9)$$

for the vibration entropy per molecule. To compare this result with the tabulated data of Ražnjević (1976), we calculate the entropy difference from Eqs. (9-4) and (9-9):

$$\Delta \Delta s = 3 \kappa k \left[\ln \left(\frac{T}{T_t} \right) + 2 A k (T - T_t) \right] \quad . \quad (9-10)$$

The comparison is shown in Fig. 6. Because the only free parameter is κ , the same conclusions about the number of degrees of freedom can be obtained from Fig. 6 as from Fig. 5.

Because of its importance in calculating the coexistence line, we also compare calculated and experimental Helmholtz free energy. This comparison requires us to define a Helmholtz free-energy difference that is a function of the internal free-energy difference, $\Delta \epsilon$, and of entropy difference, Δs :

$$\Delta f = \Delta \epsilon - T \Delta s = \Delta h - P v - T \Delta s \quad . \quad (9-11)$$

Note that, in general, $\Delta f \neq f(T) - f(T_t)$, because the entropy difference, Δs , is not zero at absolute zero temperature. Substitution of

Figure 6

Entropy per molecule of liquid water as a function of temperature.

- Experimental data from Ráznjević (1976)
- From Eq. (9-10) with $\kappa = 3$ and $\Lambda = 0$
- · - · - From Eqs. (9-4), (9-8), (7-93), and (7-101) with $\kappa = 3$
and $\Theta_i = 435.9$ K

Eqs. (9-7) and (9-10) into Eq. (9-11) yields

$$\Delta f = 3 \kappa k \left[(T - T_t) - T \ln \left(\frac{T}{T_t} \right) - A \kappa (T - T_t)^2 \right] \quad (9-12)$$

In Fig. 7 we compare Δf calculated from Eq. (9-11) and tabulated data of Ražnjević with the Δf calculated from Eq. (9-12) with $\kappa = 3$ and $A = 0$. The difference between the two curves is consistent with differences in Figs. 5 and 6.

If we consider the hydrogen molecules to be bound rigidly to the oxygen molecules, $3\alpha-6$ degrees of freedom (per cluster of molecules) are allowed for vibrational energy. Six degrees of freedom are subtracted to account for three degrees of freedom each for translation and rotation. The rigid hydrogen attachment approximation is used to calculate zero-point energies of dimers and other small clusters. See, for example, Kistenmacher et al (1974) or Braun and Leidecker (1974) who use six degrees of freedom to calculate dimer vibrational energy at $T = 0$. However, by comparing high-temperature Debye calculations of internal energy and entropy with measured values we found, for the bulk liquid phase, that there must be $9\alpha-6$ degrees of freedom per cluster of α molecules. A function, $\chi(\alpha)$, for use in Eq. (7-105) that yields the expected number of vibrational degrees of freedom, $D(\alpha)$, at $\alpha = 2$ and at $\alpha = \infty$ is

$$\chi(\alpha) = 1 - \frac{2}{\alpha} \quad (9-13)$$

Note that Eq. (9-13) is an interpolation formula and that its applicability to trimers, tetramers, etc. is conjectural.

Figure 7

Helmholtz free energy per molecule of liquid water as a function of temperature.

- Experimental data of Ražnjević (1976) and Eq. (9-11)
- - - From Eq. (9-12) with $\kappa = 3$ and $\Lambda = 0$
- · - From Eq. (9-11) with $\Delta \epsilon$ and $\Delta \Delta$ calculated from the Debye approximation (with $\kappa = 3$ and $\Theta_i = 435.9 \text{ K}$), i.e., from Eq. (7-106)

The preceding comparisons between calculated and experimental internal energy and entropy provide information about the number of degrees of freedom, 3κ , but not about the infinite medium binding energy, u_∞^I , or about the Debye temperature, Θ_i . A Debye temperature could be found from Eqs. (7-90) and (7-91); however, this would require detailed knowledge of the interparticle spacing $(V_\alpha/\alpha)^{1/3}$ and of the speed of sound of elastic waves. Because there are anharmonic effects in liquid water (that will have an effect on the speed of sound), this method may not be reliable. An alternative well-known method is finding a parameter fit to specific-heat data; however, the range of temperatures at which water is in the liquid state does not extend to values low enough for significant specific-heat variations with Debye temperature. We propose a similar method for finding the Debye temperature: instead of matching theoretical and experimental specific-heat data we will match the pressure (at low temperature) along the saturation line. This method will allow us to obtain u_i and Θ_i simultaneously.

The cluster fraction N_s/N along the coexistence line is given by Eq. (6-82). Note that at low-enough temperatures only the first term contributes to the summations. The cluster fraction from pressure and specific-volume data of Ražnjević (1976) and Eq. (6-81) is plotted in Fig. 8. The figure shows that the cluster fraction is approximately 1.0 for $T < 350$ K. For this temperature range we can approximate the summation in Eq. (6-79) for v_s , Eq. (6-80) for P_s , and Eq. (6-82) for N_s/N by taking only the first term. In this approximation, the saturation pressure from Eq. (6-80) becomes

$$P_s(T) \approx \frac{kT}{\lambda^3} e^{-(f_1^I - f_\infty^I)/kT} \quad (9-14)$$

Figure 8

Cluster fraction of water along the coexistence line.

————— Calculated from Eq. (6-81) and with pressure and specific volume data from Ražnjević (1976)

----- Calculated from Eq. (6-82)

In the high-temperature approximation the preceding equation can be written in a simple form. From Eq. (7-35) for the rotational free energy of monomers, Eq. (7-110) for the free energy of a molecule in the infinite medium, Eq. (9-1) for the free energy above the zero-point energy, Eq. (6-30) for λ , and Eq. (9-14) for $P_S(T)$ we obtain the following:

$$P_S(T) \approx e^{-[B + (3\kappa - 4) \ln T + u_\infty^i/kT]} \quad (9-15)$$

where

$$B \equiv \ln \left[k^{5/2} \left(\frac{2\pi}{h^2} \right)^{3/2} h^{-3} M^{3/2} \right] - \frac{5}{2} \ln T_1^R - 3 + 3\kappa \ln \Theta_i \quad (9-16)$$

By rearranging Eq. (9-15) we find a linear function of temperature:

$$H(T) \equiv -T \left\{ (3\kappa - 4) \ln T + P_S(T) \right\} = \frac{u_\infty^i}{k} + B T \quad (9-17)$$

We have used the saturation pressure data of Ražnjević (1976) and the rotational temperature for the monomer from Table 1 to plot $H(T)$ as a function of temperature. In the temperature range, $T = 270$ to 370 K, we find that $H(T)$ is indeed a linear function. The slope of the straight line is $B = -61.3$ and the intercept is $u_\infty^i/k = 6784$ K. The corresponding Debye temperature from Eq. (9-16) is $\Theta_i = 412.0$ K.

This Debye temperature is higher than desirable for application of the high-temperature limit, Eq. (9-1), to the vibrational free energy of liquid water in the temperature range 270 to 650 K. However, the ability of Eq. (9-15) to match the experimental data suggests that we could find

u_{∞}^i and Θ_i in an iterative procedure for the true Debye approximation, Eq. (7-106). The previously calculated values of u_{∞}^i and Θ_i provide starting guesses. We find, by repeated alternate substitution of updated values of u_{∞}^i and Θ_i into Eq. (9-14) (with a known saturation pressure at $T = 300$ K) via Eq. (7-106) for $\bar{u}_{\infty}^I$, that convergence to the following is obtained: $u_{\infty}^i/k = 5607$ K and $\Theta_i = 435.9$ K. We shall use these values for the remainder of our calculations.

We have repeated the calculation of internal energy $\Delta\epsilon$, entropy Δs , and Helmholtz free energy Δf , by using the new values of u_{∞}^i/k and Θ_i for calculating the Debye free energy from Eq. (7-93) and the internal energy from Eq. (7-101). The results are shown in Figs. 5, 6, and 7. The divergences between calculated and experimental results become greater when the Debye free energy is used than when the high-temperature limit of the Debye free energy is used. We believe that the difference is due to lack of an anharmonic correction term and that the high-temperature approximation accidentally gives better agreement.

To demonstrate the accuracy of the Debye free energy for predicting saturation-line pressure and volume at low temperature ($T \lesssim 400$ K) we have plotted the pressure from Eq. (6-80) (with one term in the summation) in Fig. 9 and the specific volume of the vapor from Eq. (6-79) (also with one term in the summation) in Fig. 10. There are two analytical results based on different free-energy calculations in each figure: (1) the infinite-medium free energy, f_{∞}^V , required by Eqs. (6-79) and (6-80), computed from the Debye free-energy equation, Eq. (7-106), with appropriate u_{∞}^i and Θ_i ; and (2) f_{∞}^V , computed from the high-temperature limit equation, Eq. (9-1), also with the appropriate previously calculated values of u_{∞}^i and Θ_i . Experimental data tabulated by Ražnjević

Figure 9

Saturation pressure of water.

- Tabulated data from Ražnjević (1976)
- From Eq. (6-80) with high temperature limit of Debye free energy, Eq. (9-1)
- From Eq. (6-80) with Debye free energy, Eq. (7-106)

Figure 10

Specific volume of water vapor along the coexistence line.

- Tabulated data from Ražnjević (1976)
- From Eq. (6-79) with high temperature limit of Debye free energy Eq. (9-1)
- From Eq. (6-79) with Debye free energy, Eq. (7-106)

(1976) are also shown in the figures. The curves in Figs. 9 and 10 imply that the two equations for the vibrational free energy of the infinite medium give similar results, but that the Debye equation, Eq. (7-106) is more accurate. The single-term representations of the series summations are very accurate for $T \lesssim 400$ K where negligible clustering occurs, but for temperatures above 400 K the calculated and experimental curves diverge. Part of the divergence is due to clustering effects and part is due to anharmonic effects.

To evaluate clustering effects we need the Debye temperature, Θ_δ , and the binding energies, u_∞^δ , for molecules on the surface of an infinite medium. The relation between surface tension and Helmholtz free energy of surface molecules given by Eq. (7-123) provides a means of determining Θ_δ and u_∞^δ . In addition to surface-tension data, $\gamma(T)$, we need information about the surface density of molecules, $\sigma(T)$. This information is indirectly provided by the specific volume (of liquid) as a function of temperature. For large clusters the number of surface molecules is given by Eqs. (7-113) through (7-115), i.e.,

$$n_\alpha^\delta = 4\pi \left(\frac{3}{4} \frac{m}{\pi} \right)^{2/3} [v_\ell(T)]^{2/3} \sigma(T) \alpha^{2/3}, \quad (9-18)$$

where $v_\ell(T) \equiv \rho_\ell(T)^{-1}$ is the specific volume of the liquid (or solid). It is reasonable to assume that the cluster will expand uniformly when heated; therefore, the number of surface molecules in a cluster of α molecules, n_α^δ , is expected to remain constant. Experimental data for $v_\ell(T)$ from Ražnjević (1976) are shown in Fig. 11. Given a surface density σ at some reference temperature and the function $v_\ell(T)$, one can determine $\sigma(T)$ at other temperatures by using of Eq. (9-18). A convenient reference temperature is 300 K; hence:

Figure 11

Specific volume of liquid water as a function of temperature. Data from Ražnjević (1976).

$$\sigma(T) = \sigma(300) \left[\frac{v_\ell(300)}{v_\ell(T)} \right]^{2/3} . \quad (9-19)$$

For convenience of notation we define a quantity $\bar{\gamma}(T)$ that is proportional to the difference in Helmholtz free energy of surface molecules and interior molecules of the infinite medium, i.e.,

$$\bar{\gamma}(T) \equiv \sigma(300) \left[f_{\infty}^s(T) - f_{\infty}^i(T) \right] ; \quad (9-20)$$

then, from Eqs. (7-123), (9-19) and (9-20),

$$\bar{\gamma}(T) = \left[\frac{v_\ell(T)}{v_\ell(300)} \right]^{2/3} \bar{\gamma}(T) . \quad (9-21)$$

If we rewrite Eq. (9-20) with the binding energies explicitly displayed,

$$\bar{\gamma}(T) = \sigma(300) \left[u_{\infty}^i - u_{\infty}^s + \tilde{f}_{\infty}^V(T, \Theta_s, A^s) - \tilde{f}_{\infty}^V(T, \Theta_i, A^i) \right] , \quad (9-22)$$

it can be proven from Eqs. (9-1) and (9-22) that, within the high-temperature limit of the Debye free energy, $\bar{\gamma}(T)$ is a quadratic function. We have used surface-tension data for water from Weast (1964, p. F-27) and from Heiks et al (1954) combined with specific volume-data from Ražnjević (1976) and Eq. (9-21) to obtain the data shown in Fig. 12. We have also constructed a linear least-squares fit to the $\bar{\gamma}(T)$ data from Weast (1964) and plotted the results in Fig. 12. The figure shows that $\bar{\gamma}(T)$ can be approximated by a linear function in the temperature range 250 to 380 K. From the least-squares fit,

$$\bar{\gamma}(T) = C_1 \left(1 - \frac{T}{T^*} \right) , \quad (9-23)$$

where $C_1 = 116.18$ dyne/cm and $T^* = 781.52$ K. Note that Eqs. (9-21) and Eq. (9-20) combine in the high-temperature approximation, to give an old well-known relationship attributed to Eötvös (1866). For an assumed Θ_δ , Eqs. (9-22) and (9-23) can be combined to obtain u_∞^δ and $\sigma(300)$. This is most easily accomplished by requiring that Eqs. (9-22) and (9-23) yield the same result at $T = T^*$ and at $T = 300$ K. The first condition yields

$$u_\infty^\delta = u_\infty^i + \tilde{f}_\infty^V(T^*, \Theta_\delta, 0) - \tilde{f}_\infty^V(T^*, \Theta_i, 0) \quad (9-24)$$

and the second yields

$$\sigma(300) = \frac{\bar{\gamma}(300)}{f_\infty^\delta(300) - f_\infty^i(300)} \quad (9-25)$$

The preceding analysis provides a method of determining u_∞^δ , the binding energy of a molecule on the surface of an infinite medium, as a function of the surface Debye temperature, Θ_δ . To determine clustering effects we also need to know the variations in binding energy of surface molecules with cluster size; hence, we employ Eq. (7-119). Instead of using p from Eq. (7-119) as a parameter, we choose to use u_2^δ , the binding energy of the dimer, as a parameter so that we can rearrange Eq. (7-119) to find an equation for p :

$$p = - \frac{\ln \left(1 - u_2^\delta / u_\infty^\delta \right)}{\ln 2} \quad (9-26)$$

The preceding analysis leaves two free parameters (u_2^δ and Θ_δ) that can be varied in a study of clustering effects. We have calculated the cluster fraction N_s/N [from Eq. (6-82) and appropriate free energies

discussed in this chapter] for several values of the parameters u_2^δ and Θ_δ . Our "best result" is shown in Fig. 8 for comparison with the experimental data from Ražnjević. For the "best result" we find $u_2^\delta/k = 1820$ K and $\Theta_\delta = 365$ K. The parameters for vibrational free energy are summarized in Table 2.

The binding energy of surface molecules from Eq. (7-119) is shown in Fig. 13. For this calculation we have used $u_\infty^\delta/k = 4581$ K and $p = 0.7304$ as determined by Eqs. (9-24) and (9-26), respectively. Results of calculations by Kistenmacher et al (1974) are also shown in Fig. 13. Although the uncertainties in the Kistenmacher et al calculations are large (~ 200 K) our calculated binding energies for small clusters are too high to give agreement within expected uncertainty; however, the qualitative agreement between the two calculations is acceptable.

Given the data in Table 2, we can compute the saturation pressure P_s from Eq. (6-80), and the specific volume v_δ from Eq. (6-79) with free energies from Eq. (7-111). The computed saturation pressure is shown in Fig. 14 for comparison with data from Ražnjević. Similarly, the computed and experimental saturation volumes are shown in Fig. 15. Comparison of Figs. 14 and 15 with Figs. 9 and 10 reveals that inclusion of higher-order terms in the summation improves agreement with experiment.

Two additional comparisons that can be made are: (1) the heat of vaporization per cluster $\ell_c(T)$, given by Eqs. (6-88) and (6-89), with the slope of the saturation pressure determined from experimental saturation-pressure data and (2) the heat of vaporization per molecule $\ell_m(T)$, given by Eq. (6-85), with the experimental heat of vaporization. These comparisons are made in Fig. 16. For calculating $\ell_c(T)$ by Eq. (6-88) we need internal energy differences defined by Eq. (6-89). They

Table 2

Parameters for calculating the vibrational free energy of liquid water. Parameters 1 and 2 are determined by matching cluster-fraction data, N_s/N . Parameters 2 through 8 are used for calculating the free energy from Eq. (7-111), (7-106), (9-15), (7-119), and (7-118). Parameters 9 through 15 are intermediate quantities.

	<u>Parameter</u>	<u>Value of Parameter</u>
1	u_2^s/k	1820 K
2	Θ_s	365 K
3	u_∞^s/k	4581 K
4	p	0.7304
5	Θ_i	435.9 K
6	u_∞^i/k	5607 K
7	α_c	34.1
8	κ	3
9	$\gamma(300)$	71.5 dyne/cm
10	T^*	781.52 K
11	$\sigma(300)$	6.458×10^{14} molecule/cm ²
12	M	18 g/mole
13	$\rho(300)$	1.0 g/cm ³

Figure 13

Binding energy per molecule.

— Calculated from Eq. (7-119) by using parameters that gave "best" match with cluster fraction data.

○ Calculated by Kistenmacher et al (1974).

Figure 14

Comparison of calculated and experimental saturation pressure of liquid water.

- Data from Ražnjević (1976)
- Calculated from Eqs. (6-80) and (7-111) with data from Table 2

Figure 15

Comparison of calculated and experimental saturation volume of liquid water.

- Data from Ražnjević (1976)
- Calculated from Eqs. (6-79) and (7-111) with data from Table 2

Figure 16

Comparison of calculated and experimental values of $l_c(T)$, the heat of vaporization per cluster, and $l_m(T)$, the heat of vaporization per molecule.

———— From data of Ražnjević (1976)
 ----- Calculated results

can be calculated with the aid of Eq. (7-101). Experimental $\lambda_g(T)$ values are expressed by using Eq. (6-86) and numerical differentiation of the saturation-pressure curve in Fig. 14, which represents data from Ražnjević (1976). The cluster fraction, N_g/N , needed for calculating $\lambda_m(T)$ from Eq. (6-85) is calculated in the same manner as previously described for the results in Fig. 8. Also needed are v_g and v_l . The specific volume of the liquid, v_l , is taken from data in Ražnjević (1976). Figures 14 through 16 show good qualitative agreement between calculations and experiment, with divergences at temperatures > 500 K. Most of this divergence is due to neglect of an anharmonic correction term in the Helmholtz free energy for vibration.

All our calculations for liquid water have been based on $\kappa = 3$; i.e., on nine degrees of freedom per molecule, the maximum value. In the solid phase the motion of the molecule is believed to be more restricted; hence, we follow a suggestion by Eisenberg and Kauzmann (1964, p. 176, 243) and postulate six degrees of freedom per molecule in the solid phase (three for center-of-mass motion about an equilibrium position and three for hindered rotation). The separation of molecules in cold water is about the same as in ice; hence, we expect the same Debye temperature for the two phases. However, the binding energy is expected to be different. We have calculated the vapor pressure above an ice surface from Eq. (6-80) and have used all the data in Table 2 except those for the binding energy of a molecule in the infinite medium, u_∞^i . By varying u_∞^i we obtain the calculated saturation pressure shown in Fig. 17. For this calculation we used $u_\infty^i/k = 5936.5$ K. Also shown in this figure are experimental data from Hilsenrath et al (1955). The figure

Figure 17

Vapor pressure of ice as a function of temperature.

- Data from Hilsenrath et al (1955)
- Calculated from Eq. (6-80) and data in Table 2 with U_{∞}^i from the table replaced by 5936.5 K

shows a very close match between calculated and experimental results over eight orders of magnitude. Our calculated binding energy of ice, $u_{\infty}^i/k = 5936.5$ K, corresponds to a sublimation energy (at $T = 0$ K) equal to 11.8 kcal/mole. Our value is slightly higher, (0.5 kcal/mole) than Eisenberg and Kauzmann's (1969, p. 101) calculated result; however, their calculation is based on a heat of vaporization equal to 11.6 kcal/mole at $T = 273.16$ K, which is also ~ 0.5 kcal/mole less than a comparable heat of vaporization that we obtain from the slope of the vapor-pressure curve [see Fig. 16], i.e., $\ell_m(273 \text{ K}) = 6100 \text{ K}$ (12.13 kcal/mole).

COMPARISON WITH EXPERIMENTS AND OTHER NUCLEATION THEORIES

In this chapter we apply our theory, derived in Chs. 2 through 8, and the numerical-free energy constants from Ch. 9 to calculate the nucleation rates for water and to compare our results with those of previous theories. We find that (without any modification of parameters) our calculated nucleation rates in a diffusion cloud chamber agree with experimental measurements within an average error margin of $\sim 10\%$. For comparison with other nucleation theories, we cast the large cluster approximation into a form that yields the classical nucleation current times an exponential factor that can be considered a correction to the classical free-energy difference of critical-size clusters. We discover that the close agreement between classical theory and experiment is an accident and that agreement is close only over the narrow temperature range accessible in diffusion cloud chamber experiments. In comparison with the Lothe-Pound theory (1967), we find that our free-energy correction factor agrees with the Lothe-Pound factor, except for an additional term that accounts in our theory for variations of cluster binding energy with cluster size. This term makes a significant contribution to the free energy and accounts for the large discrepancy between experiment and Lothe-Pound theory. We also use the free-energy constants from Ch. 9 to calculate the Schrödinger master-equation potential developed in Ch. 5. The potential function provides a new method for studying the evolution of the cluster probability distribution in time. We postulate that a plot of pressure-temperature conditions where the minimum in the

potential disappears is an upper limit of the Wilson line commonly observed in nozzle experiments.

Classical nucleation theory is used as a standard for comparison of various nucleation theories. For example, the Lothe-Pound (1969) nucleation current can be written as a free-energy correction factor, $e^{-F^{LP}/kT}$, multiplied by the classical nucleation current to obtain the predicted current; Wegener and Wu (1976) quote experimental results in terms of a factor that is multiplied by the classical nucleation current to obtain the experimental result. For the purpose of following this convention, we note that the classical nucleation current can be related to the nucleation current which, as written in Eq (5-70), constitutes our large-cluster approximation.

For further development of the large-cluster approximation, we will assume that the critical cluster-size, Γ , is large. For large clusters the internal free energy from Eqs. (7-124) and (7-114) is

$$F_{\alpha}^I(T) = \alpha f_{\infty}^I(T) + 4\pi R_1^2(T) \gamma(T) \alpha^{2/3} . \quad (10-1)$$

A combination of Eq. (5-67) with Eq. (5-44) for B_{α} and of Eqs. (5-48) and (5-55) for S indicates that the critical cluster size is determined from

$$F_{\Gamma} - F_{\Gamma-1} = f_{\infty} + kT \ln S + kT \ln \frac{A_{\Gamma}}{A_{\Gamma-1}} . \quad (10-2)$$

The number of molecules in a large critical size-cluster is [from Eqs. (10-1) and (10-2)]

$$\Gamma \approx \left[\frac{8\pi R_1(T)^2 \gamma(T)}{5 kT \lambda n S} \right]^3 \quad (10-3)$$

In the preceding derivation we assumed that the last term in Eq. (10-2) is negligible. The Zel'dovich factor from Eqs. (5-72) for Z_T , (5-65) for $B_{\mathcal{U}}/\Lambda_{\mathcal{U}}$, and (10-1) for $F_{\mathcal{U}}^I$ is

$$Z_T \approx \frac{2 R_1(T)}{5} \sqrt{\frac{\gamma(T)}{kT}} \Gamma^{-2/3} \quad (10-4)$$

Terms of order α^{-1} and higher have been dropped in the preceding derivation. For the kinetic coefficient required by Eq. (5-70) we used Eq. (8-14). Workers in classical condensation theory usually assume that the pressure is due exclusively to the presence of monomers. This is a valid assumption at temperatures low enough to neglect clustering effects near the saturation line. Hence, the number of monomers in steady state [from Eqs. (6-50) and (6-51) truncated to one term] is

$$\bar{n}_1(ss) = \frac{PV}{kT} \quad (10-5)$$

For conditions where the critical cluster size [from Eq. (10-3)] is large the large-cluster nucleation current from Eqs. (5-70) for J , (10-4) for Z_T , (8-14) for A_T (keeping only the first-order term in the series expansion), (8-13) for $\bar{v}_1$, and (10-5) for $\bar{n}_1(ss)$ is

$$J^{LC} = a_0 \frac{P(T)}{\rho(T) kT} \left[\frac{2 \pi \gamma(T)}{\pi} \right]^{1/2} S^{-1} \frac{\bar{n}_1(ss)}{V} \quad (10-6)$$

After setting $u = f_{\infty}$, as required by the supersaturated state, it can be proven from Eq. (6-58) and Eq. (10-2) without the last term, that

$$S^{\gamma-1} \bar{n}_{\gamma-1}(\text{eq}) = S^{\gamma} \bar{n}_{\gamma}(\text{eq}) \quad . \quad (10-7)$$

Hence, the large-cluster nucleation current from Eq. (10-6) is

$$J^{\text{LC}} = a_0 \frac{P}{L kT} \left[\frac{2 m \gamma}{\pi} \right]^{\frac{1}{2}} S^{\gamma} \frac{\bar{n}_{\gamma}(\text{eq})}{V} \quad . \quad (10-8)$$

Substituting the equilibrium distribution from Eq. (1-23) into Eq. (10-8) gives the large-cluster current in terms of the pseudosteady-state distribution and we recognize the result as the classical nucleation current:

$$J^{\text{C}} = a_0 \frac{P}{L kT} \left[\frac{2 m \gamma}{\pi} \right]^{\frac{1}{2}} \frac{\bar{n}_{\gamma}(\text{ps})}{V} \quad . \quad (10-9)$$

This equation is the basis of classical nucleation theory derived by McDonald (1963). A detailed comparison with classical nucleation theory requires evaluation of the pseudosteady-state distribution function, $\bar{n}_{\alpha}(\text{ps})$, for critical size clusters. In the supersaturated state $\mu = f_{\infty}^{\text{I}}$; hence, the equilibrium distribution from Eqs. (6-58), (6-32), and (7-111) is

$$\bar{n}_{\alpha}(\text{eq}) = \frac{1}{e} \left\{ F_{\alpha}^{\text{K}} + F_{\alpha}^{\text{R}} + n_{\alpha}^{\delta} \left[u_{\infty}^{\text{I}} - u_{\alpha}^{\delta} + \chi(\alpha) f_{\infty}^{\text{V}}(T, \Theta_{\delta}, A^{\delta}) - f_{\infty}^{\text{V}}(T, \Theta_{\text{I}}, A^{\text{I}}) \right] \right\} / kT \quad . \quad (10-10)$$

From Eqs. (6-52) and (5-49) we can construct the identity,

$$1 = \bar{n}_1(ss) e^{(F_1 - f_\infty^i(T) - kT \ln S)/kT} \quad (10-11)$$

If we insert the identity in the right-hand side of Eq. (10-10), use Eqs. (6-32) for F_α^K and F_1^K , (7-35) for F_α^R and F_1^R , (7-115) for n_α^δ , (7-119) for u_α^δ , (9-13) for χ , (7-110) for $f_\infty^i(T)$, (7-121) for $f_\infty^\delta(T)$, and (7-125) for γ ; we find that the pseudosteady-state distribution $\bar{n}_\alpha(ps)/V$ is

$$S \Gamma \frac{\bar{n}_\alpha(eq)}{V} = e^{-F_\alpha^{corr}/kT} \frac{\bar{n}_1(ss)}{V} e^{-(4\pi R_\alpha^2 \gamma - \alpha kT \ln S)/kT} \quad (10-12)$$

where we define

$$F_\alpha^{corr}(T) \equiv \frac{3}{2} kT \ln \left(\frac{T^R}{T_1^R} \right) - 4 kT \ln \alpha + kT \ln S + f_\infty^i(T) \\ + 4\pi R_1^2 \sigma \alpha^{(2/3 - p)} u_\infty^\delta - 8\pi R_1^2 \sigma \alpha^{-1/3} f_\infty^\delta(T) \quad (10-15)$$

If $F_\alpha^{corr} = 0$ in Eq. (10-12) we obtain the pseudosteady-state distribution that is used in classical nucleation theory [McDonald (1962)]; however, it is not obvious that F_α^{corr} is a negligible quantity; hence, classical nucleation theory is not reliable.

In addition to providing a reference calculation, classical nucleation theory provides a solvable equation for $\ln S$ that can be used as a basis for an iterative solution for S in the large-cluster approximation. If we assume that F_α^{corr}/kT is a weak function of S , Eqs. (10-8) and (10-12) can be combined and Eq. (10-3) can be used for Γ to find the following cubic equation for $\ln S$:

$$(\ln S)^3 + C_1 (\ln S)^2 + C_2 = 0 \quad , \quad (10-14)$$

where

$$C_1 \equiv \ln \left[\left(\frac{P_S}{kT} \right) \left(J\rho \right)^{-1/2} \left(\frac{2m\gamma}{\pi} \right)^{1/4} \right] - \frac{F_\Gamma^{\text{corr}}}{kT} , \quad (10-15)$$

$$C_2 \equiv - \frac{8\pi}{3} \left(\frac{m}{\rho} \right)^2 \left(\frac{\gamma}{kT} \right)^3 . \quad (10-16)$$

The solution of Eq. (10-14) that gives the correct root is:

$$\ln S = - \frac{C_1}{3} \left\{ 1 + 2 \cos \left[\frac{1}{3} \cos^{-1} \left(1 + \frac{27 C_2}{2 C_1^3} \right) + \frac{2\pi}{3} \right] \right\} , \quad (10-17)$$

The iterative solution for S in the large-cluster approximation is accomplished by simply resubstituting S and $F_\Gamma^{\text{corr}}/kT$ into Eqs. (10-17) and (10-13) with calculation of Γ from Eq. (10-5) for an intermediate step.

The most accurate method of finding J for a given S and T is by direct summation of the series in Eq. (5-58). The required free energies can be evaluated from Eq. (7-111). Several values of J can be evaluated at different T for a given S , and $S(T)$ for a specified J can then be found by interpolation. This procedure is very accurate because J is very sensitive to T . In most diffusion cloud chamber experiments, adjustments are made until a standard current, $J = 1.0$ drop/cm³s, is attained. We have solved Eq. (5-58) for $S(J=1, T)$ by using the CDC 6600 computer and the free-energy model developed for water in Ch. 9. The result is shown in Fig. 18, together with the results of the large-cluster approximation (Eq. (10-17) with $F_\Gamma^{\text{corr}} \neq 0$). The difference between the two methods of calculation is reasonably small and could be reduced by including higher-order terms in calculating, e.g., Γ and P_S .

Figure 18

Saturation ratio of water required for a current of 1.0 drop/cm³s as predicted by Eq. (5-58) and as predicted by the large-cluster approximation.

- Exact calculation by Eq. (5-58)
- Large-cluster approximation.

Next, we compare in Fig. 19 the large-cluster approximation described in the preceding paragraph and shown in Fig. 18 with the result of classical theory (dashed line) calculated from Eq. (10-17) with $F_T^{\text{corr}} = 0$. At first glance, the two results seem in close agreement; however, further analysis reveals that the agreement is probably an accident, because we see no reason for setting $F_T^{\text{corr}} = 0$ over the complete temperature range. The two curves cross at $T = 300$ K and merge approaching the critical temperature (647.3 K). As a corollary to the large-cluster approximation we obtain the correction free energy, F_T^{corr}/kT , illustrated in Fig. 20; here $F_T^{\text{corr}} (T = 300 \text{ K}) = 0$ corresponds to the crossing point in Fig. 19, with a large deviation from zero on either side of this temperature. An examination of Eq. (10-17) reveals that F_T^{corr} has no effect near the critical temperature because the surface tension, $\gamma(T)$, goes to zero at this temperature and because C_2 and $\ln S$ consequently approach zero also. Hence, the saturation ratio approaches 1.0 at the critical temperature independent of C_1 and F_T^{corr} . The agreement between classical theory and the large-cluster approximation over a wide temperature range can thus be partially explained: the two theories produced curves of similar shape with a fixed common point at $T = 647.3$ K and an accidental common point at $T = 300$ K.

Table 3 illustrates at four different temperatures the relative importance of the various terms contained in F_T^{corr} . Various large terms cancel at $T = 300$ K. The large negative values result from f_∞^i introduced by the identity, Eq. (10-11), and by $-4 \ln \Gamma$ which results from rotation and translation of critical-size clusters. The large positive contribution occurs because the zero-point energy of surface molecules is a function of cluster size. The latter information is not contained in surface-tension data obtained from infinite-medium measurements.

Figure 19

Saturation ratio of water required to produce a current, J , equal to 1.0 drop/cm³s in a diffusion cloud chamber as calculated by three methods.

- Large-cluster approximation
- - - Classical Theory
- · - Large-cluster approximation with $u_\infty^\delta = 0$ to simulate Lothe-Pound theory

Figure 20

Free-energy correction factors used to calculate saturation ratio required for a current, J , equal to 1.0 drop/cm^3 s of water in a diffusion cloud chamber.

- Used for large-cluster approximation
- Used for our calculation of Lothe-Pound prediction
- - - Katz et al (1976) equation for Lothe-Pound correction free energy using values of S and Γ determined by our Lothe-Pound calculation

Table 3

Values at various temperatures, of terms that constitute $F_{\Gamma}^{\text{corr}}(T)$ in Eq. (10-13).

T, K	Lothe-Pound Free Energy						
	Translation, Rotation, & Normalization Correction Free Energy				Replacement Free Energy		
	$\frac{3}{2} \ln \frac{T}{T_1} \frac{R}{T_1}$	$\frac{f_{\infty}^i(T)}{kT}$	$-4 \ln \Gamma$	$\ln S$	$\frac{-8\pi \sigma \Gamma^{-1/3} f_{\infty}^s}{kT}$	$\frac{4\pi R^2 \Gamma^{(2/3 - p)} U_{\infty}^s}{kT}$	$\frac{F_{\Gamma}^{\text{corr}}}{kT}$
300	-4.80	-22.77	-18.76	1.12	7.16	37.93	- 0.12
400	-4.80	-19.65	-23.89	0.43	6.22	26.21	-15.48
500	-4.80	-18.22	-28.34	0.16	5.23	19.54	-26.43
600	-4.80	-17.50	-33.50	0.05	3.92	14.99	-36.84

We have observed that the classical nucleation current is a special case of our large-cluster current with a free-energy correction term set to zero. The need for such a term has been noticed by other workers. The most famous correction term is the one proposed by Lothe and Pound (1962, 1969):

$$F_{\alpha}^{LP} = kT \ln \bar{n}_1(ss) + F_{\alpha}^K + F_{\alpha}^R - F_{\alpha}^{rep} . \quad (10-18)$$

The first term removes the incorrect normalization factor in the classical distribution, Eq. (10-12), the second is the translational free energy, Eq. (6-32), the third is the rotation free energy, Eq. (7-35), and the fourth term is called the replacement free energy, which accounts for the six degrees of freedom (three translational and three rotational) missing from the bulk free energy.

The first three terms of Eq. (10-18) can be evaluated as they had been for the derivation of Eq. (10-13) from Eq. (10-10); i.e., by using Eq. (6-52) for $\bar{n}_1(ss)$, (6-32) for F_{α}^K and F_1^K , and (7-35) for F_{α}^R and F_1^R . As a result, Eq. (10-18) can then be written

$$F_{\alpha}^{LP}(T) = \frac{5}{2} kT \ln \left(\frac{T^R}{T_1^R} \right) - 4 kT \ln \alpha \\ + kT \ln S + f_{\infty}^i(T) - F_{\alpha}^{rep}(T) . \quad (10-19)$$

Comparing Eqs. (10-13) and (10-19) reveals a similarity between F_{α}^{corr} and F_{α}^{LP} . Furthermore, note that the last term of Eq. (10-13) occurs

because the $\gamma(\alpha)$ factor in Eq. (10-10) is not unity. This factor limits the number of vibrational degrees of freedom; hence, we should consider this term the replacement free energy, i.e.,

$$F_{\alpha}^{\text{rep}}(T) = 8\pi R_1^2 \gamma \alpha^{-1/3} \tilde{f}_{\infty}^{\delta}(T) \quad (10-20)$$

From Table 3, $F_{\alpha}^{\text{rep}}(300) \approx 7 \text{ kJ}$. This is close to the Lothe-Pound (1969) estimate. Combining Eqs. (10-13), (10-19), and (10-20) yields

$$F_{\alpha}^{\text{corr}}(T) = F_{\alpha}^{\text{LP}}(T) + 4\pi R_1^2 \gamma \alpha^{(2/3 - p)} u_{\infty}^{\delta} \quad (10-21)$$

The difference between the large-cluster-approximation correction free energy and the Lothe-Pound correction free energy is the free energy that results from variation of zero-point energy of surface molecules with cluster size.

We can use the previous iterative procedure in solving for $S(J=1,T)$ predicted by the Lothe-Pound theory by taking $u_{\infty}^{\delta} = 0$ (or $p = \infty$) when calculating $F_{\alpha}^{\text{corr}}(T)$ from Eq. (10-13). The result, Fig. 19, shows that $S(J=1,T)$ predicted by the Lothe-Pound theory is considerably lower than values predicted by the large cluster approximation and by classical theory. This result is typical; see, for example, Katz et al (1976).

The correction free energy for water in the large-cluster approximation is compared in Fig. 20 to our calculation of the Lothe-Pound correction free energy from Eqs. (10-19) and (10-20), and to the Lothe-Pound correction free energy calculated by an equation from Katz et al (1976). The two calculations of the Lothe-Pound correction free energy

agree very well, but both are very different from the large-cluster approximation; hence, the last term in Eq. (10-21) is very important.

It is well known that for several different molecular species, classical nucleation theory predicts saturation ratios that agree with results of diffusion cloud-chamber experiments and that the Lothe-Pound theory predictions disagree with these experiments; see, for example, Katz et al (1976). This is true also for water, as reported by Katz and Ostermier (1967) and Heist and Reiss (1973). As previously stated, we have calculated the saturation ratio of water for a nucleation rate of $1.0 \text{ drop/cm}^3 \text{ s}$ as a function of temperature by the direct summation method, Eq. (5-58), and the result was illustrated in Fig. 18. This result is also shown in Fig. 21 for comparison with experimental measurements by Heist and Reiss (1973) and with classical theory. Results of both calculations are reasonably close to experimental values. Our direct summation method predicts a saturation ratio that averages $\sim 10\%$ less than experimental measurements.

Because the large-cluster approximation yields nearly the same result as the direct summation, we consider F_{Γ}^{corr} a much better correction free energy than F_{Γ}^{LP} . Omission of a cluster-size correction term, such as the second term of Eq. (10-21), has left a serious deficiency in an otherwise excellent attempt by Lothe and Pound (1962) to correct the classical theory.

In Ch. 5 we developed solutions of the master equation in a Fokker-Planck approximation that was converted into a Schrödinger master equation, which incorporates a potential function that provides some insight into the dynamics of the nucleation process. The Helmholtz free energies of clusters, developed for water in Ch. 9, provide the necessary

Figure 21

Comparison of calculated and measured saturation ratios required to produce a current of 1.0 drop/cm^3 s of water in a diffusion cloud chamber experiment.

- Calculated from Eq. (5-58)
- Calculated from classical theory
- Experimental result, the envelope of individual chamber-state curves from Heist and Reiss (1973)

information for evaluating growth and evaporation rates needed for constructing the Schrödinger potentials and thus for studying the nucleation of a specific system from another viewpoint. Some typical potential functions, $V(\alpha)$, from Eqs. (5-89) and (5-90) are illustrated in Figs. 22 through 25.

In Fig. 22 we illustrate $V(\alpha)$ (for $T = 300$ K and $S = 3$) as well as constituents. For large S and α , $V(\alpha) \rightarrow \bar{n}_1(ss) A_\alpha/2$, and for small S and α , $V(\alpha) \rightarrow B_\alpha/2$; therefore, we illustrate these two functions as well as $V_{\min}(\alpha)$. For most problems, the second term of $V_{\min}(\alpha)$ in Eq. (5-89) can be omitted with negligible effect. This term is of value only at very small cluster sizes, at which the Fokker-Planck approximation becomes questionable. From Fig. 22 it can be seen that A_α , the cluster growth rate, is a smooth curve, but that B_α has a rather sudden change near $\alpha = 37$. This change occurs because at $\alpha = 37$ the clusters change from those consisting entirely of surface molecules to clusters containing interior molecules. The evaporation rate decreases (as cluster size increases) at this point because interior molecules that are more tightly bound than exterior molecules are added. Because both the evaporation rate and the growth rate are proportional to the area, the slopes of A_α and B_α approach the value $2/3$ at large cluster size. In Fig. 22 we have also illustrated $V_{\min}(\alpha)$ from Eq. (5-89). This function determines the minimum value of the potential and hence the lowest eigenvalues [see Eq. (5-104)]. Except for the spike at $\alpha = 37$, $V_{\min}(\alpha)$ decreases with cluster size. The critical cluster size Γ is the value α where $V(\alpha)$ is minimum [see Eq. (5-91)]. The magnitude of Γ increases as S is lowered toward 1.0 [see Eq. (10-3)]; therefore, low values of supersaturation ($S \approx 1$) will imply small eigenvalues, Λ_1 , and very long time scales for the nucleation process.

Figure 22

Potential function for Schrödinger master equation. Constituent parts are also illustrated to demonstrate how V is constructed. Temperature, $T = 300$ K. Saturation ratio, $S = 3$.

- $V(\alpha)$ as defined by Eq. (5-90)
- · - · - $n_1(ss) A_\alpha/2$, the cluster growth rate
- - - - $B_\alpha/2$, the cluster evaporation rate
- Value of V when $\alpha = \Gamma$ as defined by Eq. (5-91)

Figure 23

Three Schrödinger master-equation potential functions defined by Eq. (5-90) demonstrate the effect of saturation ratio, S . Temperature is 300 K. Lowest eigenvalues are also shown.

————— $S = 3$
 - - - - - $S = 2$
 - · - · - $S = 1.2$

Figure 24

Three Schrödinger master-equation potentials defined by Eq. (5-90) demonstrate the effect of saturation ratio, S , at large values of S . Temperature, $T = 300$ K.

----- $S = 30$
 ————— $S = 15$
 - - - - - $S = 5$

Figure 25

Schrödinger master equation potential in Eq. (5-93) [defined by Eq. (5-90)] plotted as a function of the "spacial" variable z . Lowest eigenvalue, Λ_1 , is also shown.

The preceding conclusion is more evident in Fig. 23 in which we have plotted $V(\alpha)$ for three different saturation ratios and the same temperature (300 K). The lowest eigenvalue, Λ_1 , [see Eq. (5-104)] for each potential is superimposed on the appropriate potential. The figure illustrates that the time scale can become very long at low saturation ratio, S .

Similar plots of the potential function, $V(\alpha)$, for the large saturation ratios are illustrated in Fig. 24. At low saturation ratio, S , the potential function has a barrier between the monomer state and states represented by eigenvalues (see Fig. 25) Λ_1 ; however, at saturation ratios large enough so that $\Gamma < 37$ this barrier becomes very small and disappears when S is large enough. According to Fig. 24 this happens for $S = 30$; at this large value all clusters in the system will grow faster than they evaporate.

The natural variable of the Schrödinger master equation, Eq. (5-93), is z . When numerically solving this equation for eigenvalues the function $V(z)$ is preferred. By numerical integration we have evaluated $z(\alpha)$ from Eq. (5-80), and from this function we constructed the function $V[z(\alpha)]$ illustrated in Fig. 25.

The existence of a minimum in the potential function, $V(\alpha)$, represents a "bound" state that can be either stable or metastable. The state is stable when monomers are constantly supplied to the nucleating region, as in a diffusion cloud chamber; i.e., there is a constant probability current through the system of clusters. However, if there is no constant supply of monomers, clusters larger than Γ (the critical cluster size) will have net growth and those smaller than Γ will have net evaporation (see Fig. 22). This will allow the system to evolve to a new

metastable cluster distribution. There will be a decrease in the saturation ratio as monomers are consumed. For illustration, let us assume a constant temperature. The minimum of the potential will shift, as in Fig. 23, to successingly larger values of cluster size α , and the minimum will become smaller at a succeeding lower rate until a saturation ratio of one is reached. The equation of motion for such a system is Eq. (5-92) solved with continuously updated concentrations of monomers and with Eqs. (5-82) through (5-84) to convert wave functions to probability. If the monomer depletion is slow enough, i.e., if the inequality of Eq. (5-109) is valid, the system progresses through a series of steady-state distributions.

The disappearance of a metastable bound state, i.e., a potential minimum, from the Schrödinger master-equation potential (at high saturation ratios, see Fig. 24) can be associated with a very rapid condensation rate. This sudden increase in the condensation rate limits the saturation ratio (or pressure) that can be attained without condensation in a supersonic nozzle expansion. Because nozzle expansions are very rapid, measurements of onset pressure (the pressure at a given temperature where the first observable condensation occurs) can approach this upper limit. A set of onset pressure measurements is commonly known as the Wilson line. Points on the Wilson line of water have been measured by several authors and the results are summarized by Jaeger et al (1969). Their summary is reproduced in Fig. 26. The equation for critical cluster size, Eq. (5-91), can be solved for saturation ratio as a function of critical cluster size, i.e.,

$$S = \frac{B_{\Gamma}}{\bar{n}_1(\text{eq}) A_{\Gamma}} \quad . \quad (10-22)$$

Figure 26

Comparison of measured onset points (incidence of H_2O nucleation) with pressure determined from the maximum value of the supersaturation ratio given by Eq. (10-22).

----- $P_{S W}$ for ice
 ----- $P_{S W}$ for water

Experimental points: D Rettaliata (1936), + Yellot (1934),
 ◇ Binnie and Green (1942), Δ Binnie and Woods (1938), o Jaeger
 et al (1969), X Wegener and Pouring (1964), G Gyarmathy and Meyer
 (1965, p. 508).

----- Coexistence line

This function has a maximum value at $\Gamma = \Gamma^*$ that we denote S_w , because it represents the upper limit of a Wilson line. By using the free-energy model for water from Ch. 9 and analytic moments of inertia for clusters of three to five molecules (for smoothness) we obtain the $P_S S_w$ -versus-temperature curve illustrated in Fig. 26. At low temperature, Γ^* is the minimum value (3) allowed by this analysis; however, Γ^* becomes larger above $T = 300$ K. Results in Fig. 26 indicate that our calculated upper limit of the onset pressure is about 2.0 times higher than the measured Wilson line at temperatures of 250 to 360 K where liquid droplets are expected to form. Schaefer (1952) has verified, by using the diffusion cloud chamber, that the lowest temperature attainable for clusters in the liquid phase is 234 K. We notice a change in slope of the experimental Wilson line [see data from Jaeger et al (1969) in Fig. 26] at this temperature, indicating that the free energies of ice should be used at lower temperature. We have also shown, in Fig. 26, a calculation of $P_S S_w$ from the free energies developed for the solid phase in Ch. 9. The figure shows that both $P_S S_w$ and the measured Wilson line are higher for the solid state than values extrapolated from the upper (liquid) part of the curve. The calculation for ice is not as accurate as the one for liquid water because we were unable to obtain, from the coexistence line, the binding energy of ice dimers. The same dimer binding energy was used for both states.

CHAPTER 11

CONCLUSIONS

Most previous nucleation theories have been based on thermodynamics, on statistical mechanics, and on an assumed master equation. In our approach we have used nonequilibrium quantum statistical mechanics to derive a master equation and a complete nucleation theory from first principles; we have also compared results from our theory with experiments and with those of previous theories.

The derivation of our master equation began with a definition of an appropriate coordinate system. We chose the eigenvectors representing clusters of molecules as an orthogonal set of basis vectors in a single-particle Hilbert space $H^{(1)}$. The number of particles in the system is variable; hence, it was necessary to construct a Fock space F from the single-particle states. We defined the operation of an annihilation operator on a ket vector as removal of a particle, and determined the function of its adjoint (creation operator) in both $H^{(1)}$ and F from orthogonality and completeness relations. We proved that creation and annihilation operators common to both $H^{(1)}$ and F could be defined with certain restrictions. We identified the states in $H^{(1)}$ as system states and those in F as reservoir states. This identification allowed us to adapt quantum noise techniques from laser physics to the development of a master equation for the nucleation density operator. Operators common to $H^{(1)}$ and F permit this generalization, which is necessary because it cannot be assumed that the reservoir and system are separate entities as they are in laser physics. Hamiltonian and interaction operators that

operate in the proper spaces were obtained as expansions in terms of creation and annihilation operators. We found the equation of motion for the system density operator by tracing the master equation for the density operator over the reservoir and obtained the probability (that a cluster exists in a certain energy level) by taking the scalar product of the reduced-density-operator master equation.

The interaction operator provides the mechanism by which the system changes in time through overlap of system states (wave functions) with reservoir states. Each term of this operator is a product of system and reservoir operators. To model the nucleation process, we chose an interaction operator that is the sum of a scattering term (representing energy-level changes only) and a growth-evaporation term. The term representing scattering in the master equation becomes null, corresponding to a steady-state solution, if sufficient carrier gas is present to increase the ratio of scattering events to events that change cluster size. We found that the steady state solution of the scattering term yields a distribution for energy levels valid for both system and reservoir states. The distribution function contained constants and system variables which we were able to identify as thermodynamic variables by computing average energies and numbers of clusters and by comparing resulting equations with the Euler equation from thermodynamics. The identified variables were temperature, Boltzmann's constant, thermodynamic potential PV , and Gibbs free energy per cluster. The distribution function was recognized as the well-known distribution function for bosons. These results indicate that the laws of thermodynamics, which are based on observation, are contained in the master equation. We found that the master equation for nucleation is simplified if the

results of the steady-state scattering solution, which represent energy (but not particle) equilibrium, are reinserted into the master equation.

The probability master equation represents an infinite number of coupled differential equations. Our analysis of the master equation revealed that, over periods of time short compared to the characteristic time for monomer depletion, the cluster probabilities decay exponentially toward a distribution that is determined by a single parameter, the chemical potential. The equilibrium distribution is the same as that inferred from the law of mass action, Eq. (1-13). After proving that monomer growth and evaporation are the most likely processes we reduced the master equation to the special case of monomer processes only. This reduction allowed us to obtain a steady-state solution of the master equation. We obtained the steady-state droplet current reported by Courtney (1961) and a steady-state distribution function not previously reported. For more general solutions, we converted the master equation to a continuous Fokker-Planck equation and the Fokker-Planck equation to a Schrödinger master equation. Solutions of the Schrödinger master equation have the same type of exponential decay toward equilibrium as the general master equation; but this form contains a potential function that we analyzed to obtain the smallest eigenvalue. This eigenvalue is the decay constant for establishment of a steady-state distribution. We found that this time constant has the same form (except for a constant factor) as previous functions for the "time lag" for establishing a steady-state distribution. We also evaluated the sum in the formula for the steady-state current by the method of steepest descent to obtain a nucleation current comparable with other theories.

Our solutions of the master equation exhibit exponential decay toward a steady-state solution indicating that the nucleation process is irreversible in time; however, we started with an equation of motion for the density operator that is quantum mechanical and therefore undamped or reversible in time. Our development of the master equation from quantum noise techniques from laser physics involves the use of the Markoff approximation which, in effect, creates a memory loss in the system and thereby creates a process that is not quantum-mechanically reversible. Physically, the memory loss occurs because the time scale for collisions is much shorter than for other processes. Many collisions are required to change the reservoir; hence, although the reservoir may appear to be the same state over a relatively long period of time, it will not remain identically the same because of the collisions. Energy conservation and equilibrium reversibility between system and reservoir states, required by the delta function in the rate constants, occur without quantum-mechanical reversibility because the density of states in the reservoir is very large; i.e., the reservoir is assumed to be well approximated by a continuum of states. The derived master equation has the same form as the assumed master equation; however, the derivation establishes the limits of its validity and provides a formal method for calculating rate constants and cluster Helmholtz free energies.

Because the Euler equation from thermodynamics is contained in the distribution function (from solutions of the master equation) we were able to combine solutions of the master equation with a conservation-of-molecules equation and to outline a general method for obtaining time-dependent equations of state. After separating the kinetic part of the single-particle Hamiltonian into center-of-mass motion and into motion

relative to the center of mass, we were able to show that Bose-Einstein condensation occurs near temperatures equal to absolute zero (if there is no interaction potential) and that condensation by nucleation occurs otherwise. We have proven that, for temperatures not near absolute zero, the average number of clusters of α molecules in the $i(\alpha)^{\text{th}}$ energy level $\bar{n}_{i\alpha}$ is much less than one because the occupied states are spread over a relatively large number of energy levels. The approximation, $\bar{n}_{i\alpha} + 1 \approx 1$, greatly simplifies all equations. Boundary conditions on the translational states bring volume dependence into the distribution function. Decreasing the volume while conserving molecules reduces the number of translational states available to the system. If the volume is reduced below a critical value, i.e., the saturation volume, this removal of translational states (which are the most easily excited) forces the system to occupy zero-momentum (in the case of Bose-Einstein condensation) or cluster and bulk-phase states. We have proven, for equilibrium conditions and for volumes less than or equal to the saturation volume, that the chemical potential must become single valued and equal to the Helmholtz free energy per interior molecule to prevent divergence in the series summation for the number of molecules. It follows that the slope of a pressure-vs-volume curve is zero when the volume is less than the saturation volume. The single-valued property of the chemical potential: (1) identifies the two-phase region; (2) allows us to obtain equations for the coexistence-line functions P_s (the saturation pressure), v_s (the saturation volume), and N_s (the number of clusters); and (3) allows us to obtain the heat of vaporization per cluster and molecule as a function only of cluster Helmholtz free energies and temperature. Our result is similar to Band's, but more

general, because the Band coexistence-line functions are functions of surface tension and temperature. We were able to prove formation of a bulk phase when the volume is less than the saturation volume.

Evaluation of the Helmholtz free energy of a cluster is usually considered the most important and difficult problem in nucleation theory; however, without a clear definition of this quantity, the task is more difficult than necessary. We have defined the internal Helmholtz free energy by Eq. (6-37); it depends only on temperature and a set of eigenenergies. For evaluation of eigenenergies we have assumed negligible interaction between the vibrational and rotational parts of the Hamiltonian representing internal energy of the cluster. The rotational part was quantized by the usual procedure, and known solutions of the Schrödinger equation with the quantized operator were summarized. Formulae for calculating rotational free energy from cluster configurations and from an assumed spherical shape were presented. We have found in our numerical work that the coexistence-line functions are sensitive to monomer and small-cluster rotational free energies. For vibrations of molecules in a cluster about their equilibrium positions, we have expanded the Hamiltonian to second order (equivalent to a harmonic oscillator approximation) in generalized coordinates and followed Goldstein's transformation to a diagonal representation where the vibrational Hamiltonian could be quantized. Solutions of the Schrödinger wave equation with the quantized Hamiltonian are the expected harmonic oscillator eigenenergies. The Helmholtz free energy with the harmonic oscillator eigenenergies was evaluated by a Debye approximation. A free-energy correction factor that accounts for anharmonic effects in the vibration is added by a perturbation analysis. This correction adds

a term that is proportional to T^2 to the Helmholtz free energy. We allowed the cluster to have two Debye temperatures and binding energies per molecule: one for interior molecules and one for surface molecules. A method for calculating the number of surface molecules was developed. We find, in the large-cluster limit, that the division into surface and interior molecules leads to an energy difference that is recognized as the surface tension commonly used in other nucleation theories. An additional required function is the binding energy per surface molecule as a function of cluster size; we have used a phenomenological formula with free parameters for this part of the calculation. Our formula for the cluster free energy approaches, at large cluster sizes, the capillarity approximation. The rotational free energy, which can be reasonably well calculated, is the most important at small cluster size. The methods we have developed are more accurate than the capillarity approximation and demonstrate, from quantum-mechanical principles rather than thermodynamics, how surface tension enters into cluster free energy. Our analysis of cluster free energy presents a unified picture, which has the advantage of incorporating analytic formulae that can be used as interpolation formulae to include many types of data, such as data from small cluster molecular dynamics calculations and bulk surface tension measurements.

We have found that the transition rates are related to an absorption cross section. This relation has allowed us to use, for approximate numerical evaluation, the standard method of nucleation theory, i.e., evaluation of the kinetic coefficients in terms of a geometrical cross section times a sticking coefficient. The next logical step in theoretical development is transformation of the transition-rate

formulae to the position representation for insertion of center-of-mass translational states.

We have used our theory to study the nucleation of water. Rotational free energies were computed from calculated structure constants for small clusters and from a spherically symmetric model for large clusters. We then used bulk surface-tension data and matched our coexistence-line equations with measured data to obtain a set of vibrational free-energy parameters. The resultant phenomenological function for binding energy per surface molecule (using the determined parameters) when compared to Hartree-Fock calculations gave qualitative agreement. Without the anharmonic correction term, good agreement between measured and calculated coexistence-line functions is obtained for $270\text{ K} < T < 500\text{ K}$ with divergences above the upper limit. This temperature range covers that of available diffusion cloud chamber data. By changing the number of degrees of freedom per molecule from nine to six, by varying the binding energy of a molecule in the bulk solid, and by using the remaining previously determined parameters for water, we were able to match the calculated vapor-pressure curve of ice to the measured data over eight orders-of-magnitude variation. Advantages of obtaining the vibrational free energy by this method are: (1) a required analytical saturation pressure curve is part of the result; (2) the coexistence-line functions for the liquid phase are sensitive to free energies of clusters in the important range of 1 to ~ 100 molecules; (3) coexistence-line data can be measured very accurately, and (4) the result is an analytic function. Disadvantages are: (1) only monomer and bulk medium free energy contribute to the solid-phase vapor-pressure curve, (2) anharmonic effects make it difficult to identify causes and effects at

high temperature, and (3) the formulae are based on an incomplete understanding of the bulk liquid structure and of the liquid-to-solid phase changes.

We then used the free-energy parameters for water to calculate the droplet current in diffusion cloud-chamber experiments and an upper limit for the Wilson line in nozzle experiments. Our calculation of the cloud-chamber saturation ratio (for current equal to 1 drop/cm³s) agrees very closely with the classical-theory calculation (although the curves cross), and it lies ~10% below the measured curve. A more definitive comparison with experiment could be achieved by including anharmonic effects. The analytic form of our nucleation current (from the large-cluster approximation) was cast into the form $e^{-F^{\text{corr}}/kT}$ times the classical nucleation current, where F^{corr} is a free-energy correction factor for critical-size clusters. If F^{corr} were equal to zero our large-cluster theory would be identical with classical theory. Numerical analysis of F^{corr} vs T indicates that the curve has large variation with temperature but that it passes through zero near $T = 300$ K. We also found that all nucleation theories written in this form give a saturation ratio of unity at the critical temperature (647 K); hence, our theory and the classical theory have two common points, and the curves are very similar although the absolute value of free-energy correction factor is very large both at the critical temperature and at low temperature. Upon comparing the free-energy correction factor for the Lothe-Pound theory with ours, we found that the two factors are very similar except for an extra term in our theory that arises from cluster-size variation of the binding energy of surface molecules per surface molecule. We also used the free-energy parameters to study the potential function

of the Schrödinger master equation. This study suggested an equation for the upper limit of the Wilson line measured as the onset of condensation in nozzle flow experiments. A Wilson line compiled from several experiments is parallel to (on a semilogarithmic plot) and lies below our calculated upper limit.

Certain aspects of nucleation theory involving the formation of clusters of molecules are comparable to the formation of nuclei from nucleons (neutrons and protons). When making comparisons, we must remember that the basic particles of nuclear structure are fermions whereas our nucleation theory has been developed for bosons. Because the nucleus is composed of two types of particles, clusters in binary nucleation [see Wilemanski (1975a, 1975b)] provide a more appropriate comparison with nuclear physics than homogeneous nucleation does. Nucleation of molecules is a systems problem (including reverse reactions) in chemical reaction kinetics. The analogous nuclear-physics problem in reaction-rate kinetics is the determination of relative abundances of various nuclei at conditions of astrophysical interest. Analysis of nucleation dynamics determines that, in the Markoff approximation, reaction rates depend on two static quantities: Helmholtz free energy and average transition rates. Both depend on eigenenergies and eigenvectors that determine the structure of clusters. The static properties, i.e., cluster structure, nuclear structure, and reaction-rate constants provide another area of common interest. The liquid-drop model has served as the basic model for the "smooth" internal energy for both nuclei and clusters of molecules. The model currently plays a central role in the theory of nuclear fission where the number of nucleons in the nucleus is large (>200) [Davies, Sierk, and Nix (1976)]. As we have

found in our study, the liquid-drop model does not work well for the nucleation problem because the critical cluster size that controls the current is only a few tens of molecules, a size at which surface effects are not distinguishable because there are no "interior" molecules. A small-cluster correction term (for surface curvature) that varies with the cube root of nucleon number is used in nuclear fission calculations [see Nix (1972)]. The binding energy per nucleon from the liquid-drop model (known as the Weizsäcker formula) exhibits a maximum near nucleon numbers equal to 60, which implies that nuclei of this size should be most abundant. A more complete analysis requires inclusion of translational and rotational states and of the chemical potential for evaluation of the distribution function. The decreasing binding energy at large nuclear size [see Glasstone and Edlund (1952, p. 10)] is the result of the long-range repulsive-force term. The liquid-drop binding energy formula for clusters of molecules does not include a repulsive term and, hence, the binding energy-per-molecule curve approaches a maximum asymptotically at infinite cluster size, implying that the bulk phase is the most stable configuration. The actual distribution of clusters is determined by volume boundary conditions, which determine the chemical potential; however, at less-than-saturation volumes the bulk phase is stable. The long-range forces in nuclei produce another phenomenon in nuclei that does not occur in clusters, i.e., fission occurs in large nuclei, a phenomenon not observed in droplets. The Hartree-Fock method of solving Schrödinger's equation for both binding energies and self-consistent potential functions has proven to be a useful tool for both nuclear physics [Brown (1971, Ch. 2)] and molecular cluster physics [Kistenmacher et al (1974)]. It is the basis for the well-known shell

of the Schrödinger master equation. This study suggested an equation for the upper limit of the Wilson line measured as the onset of condensation in nozzle flow experiments. A Wilson line compiled from several experiments is parallel to (on a semilogarithmic plot) and lies below our calculated upper limit.

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structure in nuclei, another phenomenon that has not been observed in molecular clusters. Some aspects of the nucleus are described by an independent-particle model and some by collective motion of the nucleons. The independent-particle model allows the nucleons to move freely in the volume of the nucleus. The molecules in a cluster vibrate around a fixed point; however, in the harmonic-oscillator approximation these vibrations are connected by a phase factor and the result is sound waves. Second quantization of the continuum Hamiltonian for sound waves yields quanta of energy known as phonons [Fetter and Walecka (1971, p. 391)]. The phonons in the cluster (although they are bosons) have motion analogous to nucleons, described by the single-particle approximation, in the nucleus. Collective motions of the nucleus are divided into capillary surface waves and volume waves [ter Haar (1954, p. 301)]. Surface waves are considered most important in nuclear physics [Bohr (1952)]. We have made a similar division of vibrational energy by allowing different binding energies and Debye temperatures for the interior molecules and the surface molecules. The Brueckner cluster expansion and other more general cluster expansions are used to study the structure of the nucleus. Brown (1971, p. 226) has observed that the general cluster expansions are similar to the Mayer expansion in statistical mechanics. In both cases the clusters are not physically bound groups of particles, but rather represent groups of particles that are close together. In this comparison the nucleons in the nucleus are analogous to molecules in a container. Although nuclear structure is more complex than the structure of clusters of molecules, much more is known about the nucleus because clusters of uniform size are not available for detailed energy-level measurements.

Our nucleation theory has several advantages over previous nucleation theories: (1) the equations for the coexistence-line functions are an integral part of the theory, (2) the binding energy is separated from the temperature-dependent free energy, (3) unphysical Mayer clusters are avoided, (4) detailed calculations of cluster binding energy and free energy can be used when available, (5) formulae for interpolation between large- and small-cluster free energies are provided, and (6) a theoretical framework is available for inserting time-dependent forces and energy sources. The theory can be further improved by developing better methods for calculating cluster and bulk-media vibrational eigenenergies and free energies. The structure of liquid-phase clusters and the solid-to-liquid phase transitions in small clusters are not understood, although Monte Carlo calculations by Faelberer and Eters (1977) indicate their presence. Transition-rate formulae need further development so that sticking coefficients can be calculated in a manner consistent with free-energy calculations. Improved sticking coefficients may be needed for small clusters although they are ~ 1.0 for large clusters if the temperature is not too high. Recent unpublished experiments by Sibener and Lee at Lawrence Berkley Laboratory indicate that the sticking coefficient is a function of the internal energy of colliding monomers, and this effect is believed to be responsible for isotopically selective condensation [Basov et al (1975)]. These effects could be studied with our theory (because internal states are included in the development) by adding a source term to the Hamiltonian and by further theoretical development of transition-probability formulae. Better numerical agreement between theory and experiment can probably be achieved by improved and expanded Hartree-Fock calculations of small-cluster binding energies,

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by inclusion of anharmonic effects when matching coexistence-line functions to measured data, and by inclusion of a quadratic term (to include anharmonic effects) in a fit to surface-tension data. Detailed calculations of nozzle experiments using the steady-state current, the steady-state distribution function, and the equations of state that we have developed would provide an additional test of our method for calculating free energies of small clusters.

APPENDIX I

BOSE FUNCTIONS

The Bose functions (or Bose-Einstein functions) are useful in the study of Bose-Einstein condensation and in the Debye approximation for free energies of clusters. They are defined by the series

$$g_n(y) = \sum_{i=1}^{\infty} \frac{y^i}{i^n} \quad , \quad (I-1)$$

where the limits $y < 1$ and $n \geq 0$ are imposed. Special Bose functions are:

$$g_0(y) = \frac{y}{1-y} \quad , \quad (I-2)$$

and

$$g_1(y) = -\ln(1-y) \quad . \quad (I-3)$$

From the definition, the following recursion formula can be proven:

$$\frac{d}{dy} g_n(y) = y^{-1} g_{n-1}(y) \quad . \quad (I-4)$$

If the arguments are exponential functions, useful formulae are:

$$\frac{d}{dx} g_n(a e^{\sigma x}) = \sigma g_{n-1}(a e^{\sigma x}) \quad (I-5)$$

$$\int dx g_n(a e^{\sigma x}) = \frac{1}{\sigma} g_{n+1}(a e^{\sigma x}) \quad . \quad (I-6)$$

by inclusion of anharmonic effects when matching coexistence-line functions to measured data, and by inclusion of a quadratic term (to include anharmonic effects) in a fit to surface-tension data. Detailed calculations of nozzle experiments using the steady-state current, the steady-state distribution function, and the equations of state that we have developed would provide an additional test of our method for calculating free energies of small clusters.

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The Bose function $g_{3/2}(y)$ is of particular interest to condensation theory. For small arguments, the series of Eq. (I-1) converges rapidly and

$$g_{3/2}(y) \approx y \quad . \quad (I-7)$$

At the upper bound, $y = 1$, $g_{3/2}(1) = 2.612 \dots$ and the slope is infinite. A plot of the $g_{3/2}(y)$ function is shown in Fig. 27.

Figure 27

The Bose function, $g_{3/2}(y)$.

INTERACTION OPERATORS IN THE INTERACTION PICTURE

Given an interaction operator in the Schrödinger picture defined as the product of two operators: (1) $\hat{Q}_J$, in the single-particle Hilbert space $H^{(1)}$ and (2) $\hat{F}_J$ in Fock space, F , i.e.,

$$\hat{V}_J = \hat{H} \hat{Q}_J \hat{F}_J, \quad (\text{II-1})$$

we can prove that this operator in the interaction picture, previously defined by Eq. (5-14), can be written

$$\hat{V}_J(t) = \hat{V}_J e^{i \Omega_J t}, \quad (\text{II-2})$$

where Ω_J can be determined from the form of $\hat{Q}_J$ and $\hat{F}_J$. We have replaced $t - t_0$, by t to shorten the notation. The methods of proof used in this appendix are then taken from Louisell (1973, pp. 198 and 154).

We define an operator in the interaction picture as

$$\hat{O}(t) = e^{\frac{i}{\hbar} t \hat{H}_0} \hat{O} e^{-\frac{i}{\hbar} t \hat{H}_0}, \quad (\text{II-3})$$

where $\hat{O}$ is the operator in the Schrödinger picture. For $\hat{O} = \hat{V}_J$, Eq. (II-3) is the same as Eq. (3-7). The operator $\hat{H}_0$ is the single-particle Hamiltonian which, defined in terms of creation and annihilation operators, is given by Eq. (2-59). The interaction operator from Eq. (II-1) becomes, with the aid of Eq. (II-3),

The Bose function $g_{3/2}(y)$ is of particular interest to condensation theory. For small arguments, the series of Eq. 1-1 converges rapidly and

$$g_{3/2}(y) \approx \frac{4}{3} y^{3/2} \quad (1-7)$$

At the upper bound, $y = 1$, $g_{3/2}(1) = 2.612 \dots$ and the slope is infinite. A plot of the $g_{3/2}(y)$ function is shown in Fig. 27.

Figure 27

The Bose function, $g_{3/2}(y)$.

INTERACTION PICTURE IN THE INTERACTION PICTURE

Let us consider an operator in the Schrödinger picture defined as the product of two operators $\hat{O}_1$ and $\hat{O}_2$ in the single-particle Hilbert space $\mathcal{H}_1$ and $\mathcal{H}_2$ respectively, where $\hat{O}_1$ and $\hat{O}_2$ are given by

$$\hat{O}_1 = \sum_{\mathbf{k}} \hat{a}_{\mathbf{k}} \hat{a}_{-\mathbf{k}} \quad (II-1)$$

where $\hat{a}_{\mathbf{k}}$ and $\hat{a}_{-\mathbf{k}}$ are the annihilation and creation operators in the interaction picture, respectively. The operator $\hat{O}_2$ can be written

$$\hat{O}_2 = \sum_{\mathbf{k}} \hat{b}_{\mathbf{k}} \hat{b}_{-\mathbf{k}} \quad (II-2)$$

where $\hat{b}_{\mathbf{k}}$ can be determined from the form of $\hat{O}_1$ and $\hat{O}_2$. We have replaced $t = t_0$ by t to shorten the notation. The methods of proof used in this appendix are then taken from Louisell (1973, pp. 148 and 154).

We define an operator in the interaction picture as

$$\hat{O}(t) = e^{\frac{i}{\hbar} t \hat{H}_0} \hat{O} e^{-\frac{i}{\hbar} t \hat{H}_0} \quad (II-3)$$

where $\hat{O}$ is the operator in the Schrödinger picture. For $\hat{O} = \hat{V}_J$, Eq. (II-3) is the same as Eq. (3-7). The operator $\hat{H}_0$ is the single-particle Hamiltonian which, defined in terms of creation and annihilation operators, is given by Eq. (2-59). The interaction operator from Eq. (II-1) becomes, with the aid of Eq. (II-3),

$$H^{(1)} = H_0 + H_I \quad (II-4)$$

the interaction term. In the above definition,

$$H_I = H - H_0 \quad (II-5)$$

and

$$H_0 = \sum_{j=1}^N H_j^{(1)} \quad (II-6)$$

we will consider the particular case where the interaction term is linear in the creation and annihilation operators, i.e.,

$$H_I = \frac{1}{2} \left[\sum_{j=1}^N \left(a_j^\dagger + a_j \right) \right] \quad (II-7)$$

The operator, $\hat{Q}_J$, can be written in two parts:

$$\hat{Q}_J(t) = \hbar \sum_{j \in J} \left[\hat{Q}_{j1}(t) a_{j1}(t) + \hat{Q}_{j2}(t) \right] \quad (II-8)$$

The first term represents the portion of the single-particle Hamiltonian defined in $H^{(1)}$, and $\hat{Q}_{j2}(t)$ is the remainder which commutes with $\hat{Q}_J(t)$. For example, $\hat{H}_T$ could be the radiation field in a laser or the carrier gas for a set of clusters of molecules. If we define $\hat{Q}_J$ to consist of a creation and annihilation operator in $H^{(1)}$,

$$\hat{Q}_J(t) = a_{j\beta}^\dagger(t) a_{k\gamma}(t) \quad (II-9)$$

a solution for Eq. (II-7) can be found. By combining Eqs. (II-7) through (II-9) and using the commutation of $\hat{H}_r$ and $\hat{Q}_J$,

$$\begin{aligned} \frac{\partial \hat{Q}_J(t)}{\partial t} = i \sum_{i\alpha} \omega_{i\alpha} \left(a_{i\alpha}^\dagger(t) a_{i\alpha}(t) a_{j\beta}^\dagger(t) a_{k\gamma}(t) \right. \\ \left. - a_{j\beta}^\dagger(t) a_{k\gamma}(t) a_{i\alpha}^\dagger(t) a_{i\alpha}(t) \right). \end{aligned} \quad (\text{II-10})$$

Delta functions can be introduced into the above equation by using Eq. (2-34):

$$\begin{aligned} \frac{\partial \hat{Q}_J(t)}{\partial t} = i \sum_{i\alpha} \omega_{i\alpha} \left(a_{i\alpha}^\dagger(t) a_{k\gamma}(t) \delta_{ij} \delta_{\alpha\beta} \right. \\ \left. - a_{j\beta}^\dagger(t) a_{i\alpha}(t) \delta_{ki} \delta_{\gamma\alpha} \right). \end{aligned} \quad (\text{II-11})$$

The sum over i and α can be completed, Eq. (II-9) substituted into the result, and the resulting differential equation integrated to obtain:

$$\hat{Q}_J(t) = \hat{Q}_J e^{i \Omega_J^Q t}, \quad (\text{II-12})$$

where

$$\Omega_J^Q \equiv \omega_{j\beta} - \omega_{k\gamma}. \quad (\text{II-13})$$

Note that the positive sign in the above equation for Ω_J^Q is associated with the expansion coefficient, which corresponds to the creation operator in Eq. (II-9), and that the negative sign is associated with the annihilation operator.

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where $\hat{Q}_j^0$ is the initial value of $\hat{Q}_j$ at $t = 0$. Substituting Eq. (11-7) into Eq. (11-6) and using the commutation relation (11-1), we obtain

$$\begin{aligned} \frac{d\hat{Q}_j}{dt} = & \sum_{k=1}^N \left(\hat{A}_{jk} \hat{Q}_k + \hat{Q}_k \hat{A}_{kj} - \hat{A}_{kj} \hat{Q}_k - \hat{Q}_k \hat{A}_{jk} \right) \\ & + \hat{Q}_j \left(\hat{A}_{jj} + \hat{A}_{jj}^\dagger \right) + \left(\hat{A}_{jj}^\dagger + \hat{A}_{jj} \right) \hat{Q}_j. \end{aligned} \quad (11-10)$$

Equation (11-10) can be introduced into the differential equation (11-6) to obtain

$$\begin{aligned} \frac{d\hat{Q}_j}{dt} = & \sum_{k=1}^N \left(\hat{A}_{jk} \hat{Q}_k + \hat{Q}_k \hat{A}_{kj} - \hat{A}_{kj} \hat{Q}_k - \hat{Q}_k \hat{A}_{jk} \right) \\ & + \hat{Q}_j \left(\hat{A}_{jj} + \hat{A}_{jj}^\dagger \right) + \left(\hat{A}_{jj}^\dagger + \hat{A}_{jj} \right) \hat{Q}_j. \end{aligned} \quad (11-11)$$

The sum over k and j can be completed. Eq. (11-9) substituted into the result, and the resulting differential equation integrated to obtain

$$\hat{Q}_j(t) = \hat{Q}_j^0 e^{\pm \frac{\gamma_j}{2} t}, \quad (11-12)$$

where

$$\hat{Q}_j^0 \equiv \hat{Q}_j^\dagger - \hat{Q}_j. \quad (11-13)$$

Note that the positive sign in the above equation for $\hat{Q}_j^0$ is associated with the expansion coefficient, which corresponds to the creation operator in Eq. (11-9), and that the negative sign is associated with the annihilation operator.

Let $\hat{F}$ be a subalgebra of the part of the interaction operator defined in $\hat{F}$. The single-particle part of $\hat{F}$ is written as

$$\hat{F}_1 = \sum_{i,j} \hat{F}_{ij} \hat{a}_{ij}^\dagger \hat{a}_{ij} \quad (II-14)$$

In this case the $\hat{a}_{ij}^\dagger$ and $\hat{a}_{ij}$ operate on a particular set of states defined in the number representation. The $\hat{U}_p$ operators which commute with $\hat{F}_1$ are operators which operate on the states in the number representation. The $\hat{a}_{ij}^\dagger$ may or may not operate on the same single-particle states in the $\hat{a}_{ij}^\dagger$. Substitution of Eq. (II-14) into Eq. (II-6) followed by differentiation with respect to $\hat{a}_{ij}^\dagger$ yields

$$\frac{\partial \langle \hat{F}_J \rangle}{\partial \hat{a}_{ij}^\dagger} = \left(1 + e^{\frac{i}{\hbar} t \hat{H}_0} \right) \left[\hat{F}_{ij}^\dagger, \hat{F}_J \right] e^{-\frac{i}{\hbar} t \hat{H}_0} \quad (II-15)$$

If we define the portion of the interaction operator, which is in $\hat{F}$, as an arbitrary product of creation and annihilation operators,

$$\hat{F}_J = \prod_{(j\beta) \in \{j\beta\}} \prod_{(k\gamma) \in \{k\gamma\}} \hat{a}_{j\beta}^\dagger \hat{a}_{k\gamma} \quad (II-16)$$

the commutation rules or Eq. (2-52) and Eq. (2-53) can be used to evaluate the commutator of Eq. (II-15). The products in the above equation are to be executed over a set of symbols (not numbers) associated with a specific interaction identified by the argument, J . Set $\{j\beta\}$ identifies the creation operators and Set $\{k\gamma\}$ identifies the annihilation operators. If $m\delta \in \{j\beta\}$

$$[b_{m\ell}^-, b_{m\ell}^-, \hat{F}_J] = -\hat{F}_J \quad \text{II-17}$$

Substitution of Eqs. (II-16) and (II-17) into the above equation produces the following result:

$$[b_{m\ell}^-, b_{m\ell}^-, \hat{F}_J] = \hat{F}_J \quad \text{II-18}$$

Analogously, if $m\ell \in \{k\gamma\}$,

$$[b_{m\ell}^-, b_{m\ell}^-, \hat{F}_J] = -\hat{F}_J \quad \text{II-19}$$

Substitution of Eqs. (II-18) and (II-19) into Eq. (II-15) produces a differential equation,

$$\frac{\partial \hat{F}_J(t)}{\partial \omega_{m\ell}} = \pm 1 \pm \hat{F}_J(t) \quad \text{II-20}$$

where the positive sign applies if $m\ell \in \{j\beta\}$ and the negative sign applies if $m\ell \in \{k\gamma\}$. The operator, $\hat{F}_J$, is a function of all the expansion coefficients contained in $\{j\beta\}$ or $\{k\gamma\}$; therefore, the total differential is

$$d\hat{F}_J(t) = \sum_{\{m\ell\}(J)} \frac{\partial \hat{F}_J(t)}{\partial \omega_{m\ell}} d\omega_{m\ell} \quad \text{(II-21)}$$

A combination of Eqs. (II-20) and (II-21) produces

Next, we shall consider the portion of the interaction operator defined in F . The single-particle Hamiltonian can also be written as

$$\hat{H}_0 = \hbar \sum_{i\alpha} \omega_{i\alpha} \bar{b}_{i\alpha} b_{i\alpha} + \hat{H}_r. \quad (\text{II-14})$$

In this case the $\bar{b}_{i\alpha}$ and $b_{i\alpha}$ operate on a particular set of state vectors in the number representation. The $\hat{H}_r$ operators which commute with $\hat{F}_J$ may represent another set of state vectors in the number representation. The $b_{i\alpha}$ may or may not operate on the same single-particle states as the $a_{i\alpha}$. Substitution of Eq. (II-14) into Eq. (II-6) followed by differentiation with respects to $\omega_{m\delta}$ yields:

$$\frac{\partial \hat{F}_J(t)}{\partial \omega_{m\delta}} = i t e^{\frac{i}{\hbar} t \hat{H}_0} \left[b_{m\delta}^+ b_{m\delta}, \hat{F}_J \right] e^{-\frac{i}{\hbar} t \hat{H}_0}. \quad (\text{II-15})$$

If we define the portion of the interaction operator, which is in F , as an arbitrary product of creation and annihilation operators,

$$\hat{F}_J = \prod_{\{j\beta\}(J)} \prod_{\{k\gamma\}(J)} b_{j\beta}^+ b_{k\gamma}, \quad (\text{II-16})$$

the commutation rules or Eq. (2-52) and Eq. (2-53) can be used to evaluate the commutator of Eq. (II-15). The products in the above equation are to be executed over a set of symbols (not numbers) associated with a specific interaction identified by the argument, J . Set $\{j\beta\}$ identifies the creation operators and Set $\{k\gamma\}$ identifies the annihilation operators. If $m\delta \in \{j\beta\}$

$$[b_{m0}, \hat{F}] = [b_{m0}, \hat{F}_J] = \hat{F}_J b_{m0} - b_{m0} \hat{F}_J \quad \text{II-17}$$

Using the commutation rule of Eq. II-11, the above equation, and Eq. II-17, we can write

$$[b_{m0}^{\dagger}, b_{m0}, \hat{F}_J] = \hat{F}_J \quad \text{II-18}$$

Similarly, if $m \in \{k\}$,

$$[b_{m0}^{\dagger}, b_{m0}, \hat{F}_J] = -\hat{F}_J \quad \text{II-19}$$

Substitution of Eqs. II-18 and II-19 into Eq. II-15 produces a differential equation,

$$\frac{\partial \hat{F}_J(t)}{\partial \omega_{m0}} = \pm i t \hat{F}_J(t) \quad \text{II-20}$$

where the positive sign applies if $m \in \{j\}$ and the negative sign applies if $m \in \{k\}$. The operator, $\hat{F}_J$, is a function of all the expansion coefficients contained in $\{j\}$ or $\{k\}$; therefore, the total differential is

$$d\hat{F}_J(t) = \sum_{\{m0\} \in \{J\}} \frac{\partial \hat{F}_J(t)}{\partial \omega_{m0}} d\omega_{m0} \quad \text{II-21}$$

A combination of Eqs. (II-20) and (II-21) produces

$$= \sum_{j=1}^{\infty} \sum_{k=1}^{\infty} \left| \frac{1}{k!} \left(\frac{\partial}{\partial \alpha} \right)^k \right| \dots$$

where $\alpha = \alpha_j$.

$$= \sum_{j=1}^{\infty} \sum_{k=1}^{\infty} \left| \frac{1}{k!} \left(\frac{\partial}{\partial \alpha} \right)^k \right| \dots \quad \text{II-27}$$

and

$$\sum_{j=1}^{\infty} \sum_{k=1}^{\infty} \left| \frac{1}{k!} \left(\frac{\partial}{\partial \alpha} \right)^k \right| \dots \quad \text{II-28}$$

where

$$= \sum_{j=1}^{\infty} \sum_{k=1}^{\infty} \left| \frac{1}{k!} \left(\frac{\partial}{\partial \alpha} \right)^k \right| \dots \quad \text{II-29}$$

Eq. (II-27) and Eq. (II-28) for $\hat{Q}_j(t)$, Eq. (II-29) for $\hat{F}_j(t)$ and Eq. (II-26) for $\hat{H}_j$, combine to give Eq. (II-2), which is the final result.

After $\hat{H}_j$ is chosen for a particular application, $\hat{Q}_j$ can be determined by inspection of the form of $\hat{H}_j$. The limitations of $\hat{Q}_j$ implied by Eq. (II-2) must be considered when $\hat{H}_j$ is chosen. There are no limitations on the form of $\hat{F}_j$ as Eq. (II-16) implies. This lack of limitations is a consequence of being able to use the commutation rule creation and annihilation operators in $\hat{F}$.

SOLUTION OF THE SCHRÖDINGER MASTER EQUATION

The time evolution of a set of clusters (when there is a constant monomer density) can be studied by solving the Schrödinger master equation, Eq. (5-85). If we define a Liouville operator as

$$L \equiv \frac{1}{2} \frac{\partial^2}{\partial z^2} - V(z) \quad , \quad (\text{III-1})$$

the Schrödinger master equation, Eq. (5-85), can be written as

$$\frac{\partial u(z,t)}{\partial t} = L u(z,t) \quad . \quad (\text{III-2})$$

By separation of variables the solution of the preceding equation is

$$u(z,t) = \sum_I C_I e^{-\Lambda_I (t - t_0)} \psi_I(z) \quad , \quad (\text{III-3})$$

where Λ_I is an eigenvalue and $\psi_I(z)$ is the corresponding continuous eigenvector obtained by solving

$$L \psi_I(z) = -\Lambda_I \psi_I(z) \quad . \quad (\text{III-4})$$

The C_I is an expansion coefficient. In addition to Eq. (III-4) there is an adjoint equation,

where λ_i and λ_j are eigenvalues of L and L^* respectively.

$$c_{ij} = \int_{\Omega} \psi_i \psi_j^* d\Omega \quad (III-8)$$

The adjoint of L is defined by

$$L^* \psi_j = \lambda_j^* \psi_j^* \quad (III-9)$$

$$L^* \psi_j = \lambda_j^* \psi_j^* \quad (III-10)$$

and

$$L^* \psi_j = \lambda_j^* \psi_j^* \quad (III-11)$$

where λ_i and λ_j are complex numbers. The adjoint of L , L^* , is the complex conjugate of L . Moreover, $L^* = L$ if L is self-adjoint.

$$c_{ij} = \int_{\Omega} \psi_i \psi_j^* d\Omega \quad (III-12)$$

The eigenvectors are orthogonal. To prove this we apply Eqs. (III-4) and (III-5) to Eq. (III-10) and use Eq. (III-9) to obtain

$$(\lambda_i - \lambda_j^*) c_{ij} = 0 \quad (III-11)$$

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differentiation of Eq. (III-3) yields:

$$L^{\dagger} L = L L^{\dagger} = 0 \quad (III-3)$$

(III-3)

By the definition of the adjoint, we define the adjoint of L by

$$\langle \phi, L \psi \rangle = \int d^3x \phi^{\dagger} L \psi \quad (III-4)$$

(III-4)

For the definition of $L^{\dagger}$ we require

$$\langle L^{\dagger} \phi, \psi \rangle = \langle \phi, L \psi \rangle \quad (III-5)$$

(III-5)

$$L^{\dagger} \phi = \int d^3x \phi^{\dagger} L \psi \quad (III-6)$$

(III-6)

and

$$\langle \phi, L \psi \rangle = \langle L^{\dagger} \phi, \psi \rangle \quad (III-9)$$

(III-9)

where α and β are complex numbers. The adjoint of L , $L^{\dagger}$ has the property (Merzbacher 1941, p. 341):

$$\langle \phi_J, L \phi_I \rangle = \langle L^{\dagger} \phi_J, \phi_I \rangle \quad (III-10)$$

(III-10)

The eigenvectors are orthogonal. To prove this we apply Eqs. (III-4) and (III-5) to Eq. (III-10) and use Eq. (III-9) to obtain

$$(A_I - A_J) \langle \phi_J, \phi_I \rangle = 0 \quad (III-11)$$

(III-11)

If the eigenvalues are unique, it follows that

$$(\phi_J, \psi_I) = (\phi_I, \psi_I) \delta_{IJ} \quad . \quad (\text{III-12})$$

To find the effect of L operating on ϕ_J , we take the scalar product of ψ_I^* with $L\phi_J$, use the definition, Eq. (III-6), integrate by parts, and use Eqs. (III-4), (III-9), and (III-8) to obtain

$$(\psi_I^*, L\phi_J) = -\Lambda_I(\psi_I^*, \phi_J) + \psi_I(z)^2 \left(\frac{\phi_J(z)}{\psi_I(z)} \right) \Big|_0^\infty \quad . \quad (\text{III-13})$$

If we impose the boundary condition that $\psi_I(0) = \psi_I(\infty) = 0$, it follows that:

$$L \phi_J = -\Lambda_J \phi_J \quad . \quad (\text{III-14})$$

By comparing this result with Eq. (III-4), it follows that the vectors ψ_I and ϕ_I are isomorphic; hence, we can write Eq. (III-12) as

$$(\psi_I, \psi_J) = (\psi_I, \psi_I) \delta_{IJ} \quad . \quad (\text{III-15})$$

Existence of a nonzero infinite-time solution of Eq. (III-2) requires that the lowest eigenvalue be zero. At $t = \infty$ the time rate of change is zero; hence, we obtain from Eq. (III-2),

$$L u(z, \infty) = 0 \quad . \quad (\text{III-16})$$

Differentiation of Eq. (III-3) yields:

$$-\sum_I C_I \Lambda_I e^{-\Lambda_I (t - t_0)} \psi_I(z) \Big|_{t=\infty} = 0 \quad . \quad (\text{III-17})$$

From the preceding equation it is evident that the equality can only be satisfied if the real part of $\Lambda_I \geq 0$. Taking the lowest eigenvalue, $\Lambda_0 = 0$, allows us to rewrite Eq. (III-3) as

$$u(z, t) = C_0 \psi_0(z) + \sum_{I=1}^{\infty} C_I e^{-\Lambda_I (t - t_0)} \psi_I(z) \quad . \quad (\text{III-18})$$

From Eq. (III-18) at $t = \infty$, it follows that

$$C_0 \psi_0(z) = u(z, \infty) \quad . \quad (\text{III-19})$$

To evaluate the expansion coefficients, we substitute Eq. (III-19) into (III-18); take the scalar product of Eq. (III-18) evaluated at $t=t_0$ with $\psi_J(z)$; and use the orthogonality condition, Eq. (III-15), to complete the summation. After resubstitution of the result into Eq. (III-18) the solution for $u(z, t)$ is .

$$u(z, t) = u(z, \infty) + \sum_{I=1}^{\infty} \frac{(\psi_I, u(t_0))}{(\psi_I, \psi_I)} \psi_I(z) e^{-\Lambda_I (t-t_0)} \quad . \quad (\text{III-20})$$

The function $u(z, \infty)$ [or $\psi_0(z)$] is determined by solution of the second-order ordinary differential equation, Eq. (III-16). Note that C_0 cannot be determined; however, it is not necessary to know this quantity. The solution, Eq. (III-20), is similar to Eq. (5-21) for the probability distribution. The major difference is: the infinite-time probability

distribution for Eq. (III-20) is obtained from a single operator equation rather than from a set of disconnected equations. The function $u(z,t)$ is derived under the assumption of a constant supply of monomers; hence, $u(z,\infty)$ is a steady-state distribution and should be replaced by $u(z,ss)$.

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