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THEORY OF PHASE SEPARATION IN
QUANTUM CRYSTAL ALLOYS

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Abstract

Solid mixtures of isotopic helium separate into a He^3 -rich phase and a He^4 -rich phase at temperatures below 0.5°K and near melting pressure. This phenomenon was understood since I. Prigogine as a result of the volume effect due to the different zero-point kinetic energies of the two isotopic atoms in the mixture. A semi-classical theory was proposed by W. Mullin in which the volume effect was taken into account. We propose a theory based on first principles of the quantum mechanics and this theory contains Mullin's theory as a special case.

We start our theory with a set of localized states, in one of such states each atom is localized around a lattice site. The proper states of the solid mixture are described by linear combinations of these localized states. The free energy and henceforth other thermodynamic properties are obtained by calculating the energy and the entropy of the solid mixture, utilizing our localized states. We propose two mutually equivalent methods to calculate the energy and entropy. In the first method we make use of a combinatorial analysis which inspires us to the invention of the second method in which we calculate the free energy within a restricted ensemble. Both methods yield correct thermodynamics of the phase separation. The quantities involved in the expression of the free energy are full many-body integrals with a clear physical meaning: each site is partially occupied by a He^3 .

wavefunction and partially by a He^4 wavefunction. This result may hopefully explain why the exchange energies in a mixture solid helium do not depend on He^3 concentration strongly.

Chapter 1

Introduction

Quantum crystals¹⁾ are those whose composed atoms perform large zero-point motion. Helium solids are typical among the quantum crystals; their zero-point amplitude reaches about one third of the lattice spacing. Many striking features can be inferred from the large zero-point motion. For instance, they occupy a larger volume than that predicted by the theory of classical lattice dynamics.²⁾ A consequence of the large zero-point motion is that the atoms can tunnel through the potential barriers separating them and exchange their positions, at a relatively high frequency.³⁾ The large volume and frequent exchange are the major reasons of the phase separation of a $\text{He}^3\text{-He}^4$ solid mixture, which is the essential topic of this paper.

In 1962, Edwards, McWilliams and Daunt discovered experimentally⁴⁾ that a solid mixture of He^3 and He^4 undergoes a phase separation at temperatures below 0.5°K, when the solid pressure is not too far from its melting pressure. One of the two separated phases is rich in He^3 , and the other is rich in He^4 . This phenomenon was identified by a peak in the specific heat at the phase separation temperature.

The cause of this phase separation has been understood since Prigogine.⁵⁾ The interaction between any pair of isotopic helium atoms is the same. Because at the densities of a solid phase (lattice distance ~ 3 to $4 \text{ \AA}$), the interaction between any pair of helium atoms is determined by their electronic structure, which

is identical for both isotopes. However, the kinetic energies of a He^3 and a He^4 atoms are different. The zero point kinetic energy is inversely proportional to the isotopic mass. Therefore, a He^3 atom has higher kinetic energy than a He^4 atom in a solid, and thus needs a larger space. In fact, due to zero-point effects, the molar volume of a pure He^3 solid is 24.4 c.c. and that of a pure He^4 solid is only 20.4 c.c. at $P = 36$ atm.

A He^3 atom finds itself in a smaller volume in a mixed phase, than in the pure phase. Therefore, the zero-point energy of a He^3 atom in a mixed phase is larger than in the pure phase. But a He^4 atom finds itself in a larger volume in a mixed phase, and therefore its zero-point energy in a mixed phase is lower. However, the excess in the He^3 zero-point energy exceeds the reduction in the He^4 zero-point energy. In other words, the absolute value of the first derivative of the He^3 energy with respect to the He^3 concentration, or the partial pressure exerted by the He^3 atoms is higher than the first derivative of the He^4 energy with respect to the He^4 concentration, or the partial pressure exerted by the He^4 atoms. Furthermore, there is every reason to expect that the second derivatives of the energies, or the partial compressibilities are unequal, as was pointed out by Mullin⁶⁾ in an earlier theory.

Now that the energy of separated phases is lower than that of a mixed phase as in the case of helium solids, phase separation happens at a finite temperature. Since we are looking to whether separated phases or a mixed phase has lower free energy ($F = U - TS$). And at very low temperatures, the energy part U in the free energy F

dominates. We shall leave the details of the thermodynamics⁷⁾ to Chapter 4.

Thus far we have only considered the zero temperature energy. What about the thermal energy due to excitations? Well, since we are interested in a temperature region of say, below 0.5°K, the thermal energy (primarily due to phonons) will give an amount of the order of $KT(\frac{T}{\theta_D})^3$, where θ_D is the Debye temperature of the solid. θ_D equals 20°K approximately so the thermal energy will amount at most to

$$0.5 \left(\frac{0.5}{20} \right)^3 \sim 10^{-5} \text{ } ^\circ\text{K} ,$$

which is about five orders smaller than the zero temperature energy and therefore is negligible.

Now let us discuss the mechanism through which the equilibrium of phase separation is established. At the phase separation temperatures $T \leq 0.5^\circ\text{K}$, the thermal diffusion energy of a helium atom from one site to its nearest neighbor site is of the order of

$$\phi e^{-\phi/KT} \leq (10^\circ\text{K}) e^{-10/0.5} \sim 10^{-7} \text{ } ^\circ\text{K} \quad (1-1)$$

where ϕ is approximately the height of a single particle energy well in the crystal. But the exchange energy between a $\text{He}^3\text{-He}^4$ pair is at least $10^{-5} \text{ } ^\circ\text{K}$,⁸⁾ which is two-order higher than thermal diffusion, and therefore, dominates. The equilibrium of the phase separation is therefore established through the relatively frequent

tunnelling process. The tunnelling frequency is thus

$$\omega = \frac{\epsilon}{\hbar} \sim 10^6/\text{sec} \quad (1-2)$$

A typical macroscopic dimension is about 10^7 to 10^8 atoms per side. We can thus estimate the relaxation time of reaching an equilibrium during phase separation:

$$\tau \sim \frac{10^7 \text{ to } 10^8}{10^6} \sim 10 \text{ to } 100 \text{ sec.} \quad (1-3)$$

To calculate the thermodynamic properties of a mixture solid, let us consider a particular arrangement C of the atoms on their sites, and consider the phonon states this arrangement gives. (See Figure 1)

Each phonon state is labeled by $|n(c), c\rangle$. Now, we can generate different arrangements through permuting these particles over their sites. Since all the He^4 atoms are indistinguishable, and all the He^3 atoms with the same spin considered the same, we find out that there can be

$$2^{N_3} \cdot \frac{N!}{N_3! N_4!}$$

different arrangements. The thermodynamics of the system is therefore, generated from the partition function

$$Z = \sum_c \sum_{n(c)} e^{-\beta E_n(c)} \quad (1-4)$$

Since

$$\sum_{n(c)} e^{-\beta E_n(c)} = e^{-\beta \left[E_0(c) + K(c) \frac{T^4}{\theta_0(c)^3} \right]} \approx e^{-\beta E_0(c)} \quad (1-5)$$

for $T \leq 0.5^\circ\text{K} \ll \theta_0(c) \sim 20^\circ\text{K}$, which is the temperature region we are interested in, we shall approximate (1-4) by

$$Z \approx \sum_c e^{-\beta E_0(c)} \quad (1-6)$$

Our calculations are based on equation (1-6). We use a restricted ensemble which, in the required thermodynamic limit, is equivalent to the canonical ensemble (see Appendix A). The entire derivation of the free energy is described in Chapter 3.

We shall also present our original derivation of the free energy in Chapter 2. This derivation involves a long combinatorial analysis which forms an interesting mathematical problem by itself. We present this original derivation not only for the sake of historical completeness, but also for showing the many efforts we have paid to solve the solid mixture problem and how it eventually leads to our later derivation (Chapter 3).

In Chapter 4 we present the thermodynamics and the numerical results, which are no different from those obtained by Mullin⁶⁾, who derived the free energy of the helium solid mixture based on a

simpler theory. In his theory Mullin assumed that He^3 and He^4 atoms are randomly distributed throughout a perfect bcc lattice, in each of the separated phases. With this assumption, he carried out a cluster expansion truncated after the two-body terms to evaluate the ground state energy of the solid mixture. In his theory no information was given to the contribution due to the other atoms outside the two atoms under consideration. More importantly, his assumption of random distribution remains a mystery which is finally resolved in our theory. Further, the cluster expansion method Mullin used is not justified.

In Chapter 5, we shall therefore discuss Mullin's theory and give a critique to it. We shall see that Mullin's result can be considered as the limit of our expression for the free energy, when taking the two-body approximation.

A discussion on whether lattice distortion is important is also included in Chapter 5.

Generally speaking, this theory of phase separation applies to any quantum and classical crystal alloys. Escaping from reality to fantasy, imagine a possible solid phase of neutron-proton mixture in the neutron stars. Neutrons form solids (if they do) which are even more quantumic than helium solids.⁹⁾ Would it then be an interesting question, whether the neutron - proton solid mixture in the stars phase separates, and if so, at what temperatures?

Chapter 2

Free Energy as the Solution to a Combinatorial Problem

Let us consider a system of N_3 He^3 atoms and N_4 He^4 atoms forming a lattice solid. $N (= N_3 + N_4)$ is the total number of the atoms, which is expected to be equal to the number of lattice sites. In other words, we expect the vacancy concentration to be negligible and double occupancy has a very rare possibility. Assuming no zero-point vacancies, the vacancy concentration at the phase separation temperature is about¹⁰⁾

$$e^{-\phi_V/T} \leq e^{-10/0.5} \sim 10^{-8}$$

and the double occupancy probability is at most of this order.

The contributions to the energy and entropy of such a crystalline mixture due to the excited states (primarily phonon states) are expected to be extremely small at phase separation temperatures. Both of them amount at most to the order of $(\frac{T}{\theta_D})^3$ or $(\frac{0.5}{20})^3 \sim 10^{-5}$ of the ground state energy and the entropy of mixing. Thus the dominant components in the free energy F are the ground state energy E_g and the entropy of mixing S_m :

$$F = E_g - T S_m \quad (2-1)$$

We shall calculate E_g and S_m through a microscopic approach. The hamiltonian of the mixture system may be written as

$$\begin{aligned}
H = & \sum_{i=1}^{N_3} -\frac{\hbar^2}{2m_3} \nabla_i^2 + \sum_{i=N_3+1}^{N_3+N_4} -\frac{\hbar^2}{2m_4} \nabla_i^2 + \sum_{1 \leq i < j \leq N_3} v_{33}(r_{ij}) \\
& + \sum_{\substack{1 \leq i \leq N_3 \\ N_3+1 \leq j \leq N}} v_{34}(r_{ij}) + \sum_{N_3+1 \leq i < j \leq N} v_{44}(r_{ij}) \quad (2-2)
\end{aligned}$$

where we have assumed slightly different potential energies between different isotopic atoms, as was recently reported by Bennewitz et.al.¹¹⁾ Consider those eigenstates of H with the proper symmetry (He^3 atoms obey fermi statistics and He^4 atoms obey bose statistics) representing a solid mixture of a certain lattice structure (say b.c.c.). Let us denote these lattice states with the proper statistical symmetry by $|m\rangle$. Each state $|m\rangle$ should obey the translational symmetry of the lattice. Therefore, in a state $|m\rangle$, each atom is not localized at one site and instead has almost equal probability of wobbling around every site. Let the lowest state among $\{|m\rangle\}$ (the ground state) be $|g\rangle$. Then the ground state energy of the solid mixture may be expressed as

$$E_g = \frac{\langle g | H | g \rangle}{\langle g | g \rangle} \quad (2-3)$$

Since in $|g\rangle$ the atoms are not localized, it is not technically easy to start with $|g\rangle$ to Solve Eq. (2-3). However, we can consider a set of localized states $\{|n(c), c\rangle\}$ obtained by linearly super-imposing the low-lying states $|m\rangle$:

$$|n(c), c\rangle = \sum_m C_{n(c), c; m} |m\rangle \quad (2-4)$$

In a state $|n(c), c\rangle$, each atom is localized around a lattice site. Let us forget about the label $n(c)$ for a while. The label C denotes a particular arrangement or configuration of the atoms on the lattice sites (see Fig. 1). By permuting the particles on their sites, we can generate one state having a certain arrangement of atoms to another state. Permuting identical particles does not generate a new state. Since all the He^3 atoms with the same spin are indistinguishable, and all the He^4 atoms are identical, we can see that there can be

$$\Omega \equiv 2^{N_3} \cdot \frac{N!}{N_3! N_4!} \quad (2-5)$$

such states. The index $n(c)$ in $|n(c), c\rangle$ denotes an energy level for a particular arrangement C . Let the lowest state for each configuration C be $|0(c), c\rangle \equiv |c\rangle$, and the excited states be $|n(c), c\rangle$, $n(c) = 1, 2, 3, \dots$. These excited states $|n(c), c\rangle$ ($n(c) > 0$) contribute only a negligible amount to the free energy, as we have argued before. Therefore, we shall consider only the lowest states $|c\rangle$ for all of the arrangements. To calculate the ground state energy, we need only to consider these lowest states $|c\rangle$.

The ground state wavefunction can be constructed in the following way. First, super-impose linearly the $|c\rangle$ states, with all the coefficients having unit modula. This way we obtain a

spatial part. Multiply the spatial part by a spin part. Then symmetrize the He^4 coordinates and antisymmetrize the He^3 coordinates in the total wavefunction. This construction does not give a unique wavefunction. The ground state is then the lowest state among those constructed states.

$$\langle \vec{r}_1, \sigma_1 \mid g \rangle = \frac{1}{\Omega} a_3 S_4 \sum_c c_{c,g} \langle \vec{r}_1 \rangle \langle c \mid \chi(\{\sigma_1\}) \rangle \quad (2-6)$$

where a_3 and S_4 are antisymmetrizer (on the He^3 coordinates) and symmetrizer (on the He^4 coordinates) respectively. $\chi(\{\sigma_1\})$ is the spin wave function of the He^3 atoms.

Now, since symmetrizing the He^4 coordinates and antisymmetrizing the He^3 coordinates only give a correction to the ground state energy within one part of a thousand, and since the total contribution from the off-diagonal integrals, that is, $\langle c' \mid H \mid c \rangle$ and $\langle c' \mid c \rangle$ ($c' \neq c$), gives 10^{-3} of the diagonal ones,¹²⁾ we can simply propose the formula for the ground state energy as

$$E_g = E_0 + 0 (10^{-3} E_0) \quad (2-7)$$

where

$$E_0 = \frac{\sum_c \langle c \mid H \mid c \rangle}{\sum_c \langle c \mid c \rangle} \quad (2-8)$$

We shall devote the entire later half of this chapter to a combinatorial analysis which leads to the solution of Eq. (2-8).

Before we do so let us calculate the term $-T S_m$.

$$S_m = K \ln \Omega = K \ln \left\{ 2^{N_3} \frac{N!}{N_3! N_4!} \right\} \quad (2-9)$$

By applying Stirling's formula to Eq. (2-9), for large N , N_3 and N_4 , and keeping in mind that $x \equiv \frac{N_3}{N}$ and $1-x \equiv \frac{N_4}{N}$, we obtain

$$-T S_m = NKT \{ -x \ln 2 + x \ln x + (1-x) \ln(1-x) \} \quad (2-10)$$

Now we start to solve for E_0 in Eq. (2-8). First, we shall not consider the spins of the He^3 atoms. Because the difference in the spins contributes a term $xNK \ln 2$ in the entropy, and contributes nothing to E_0 . Secondly, for the convenience in our analysis, we shall write the numerator of Eq. (2-8) in the form of

$$\frac{1}{\Omega'} \sum_c \sum_{p(c)} \langle p(c) | H | p(c) \rangle \equiv \frac{1}{\Omega'} \sum_p \langle p | H | p \rangle ,$$

where

$$\Omega' = \frac{N!}{N_3! N_4!} \quad \text{and} \quad |p(c)\rangle$$

is a sub-state of $|c\rangle$: permuting identical particles on the sites gives a different $|p(c)\rangle$, belonging to the same $|c\rangle$. Since physically all of the sub-states $\{|p(c)\rangle\}$ represent the same state $|c\rangle$, these sub-states are fictitious states and only exist mathematically.

We shall make use of two lemmas in the course of our analysis. The readers may find the proofs in Appendix B.

The trial wavefunction we shall use in our variational calculation is in the form of a product of single particle wavefunctions of the Gaussian type multiplying a product of two-body correlation functions of the Jastrow type:

$$\langle \{\vec{r}_i\} | p \rangle = \phi_p \mathcal{F} \quad (2-11)$$

where

$$\phi_p = \prod_{i=1}^{N_3} \phi_3(|\vec{r}_{p1} - \vec{R}_i|) \prod_{i=N_3+1}^N \phi_4(|\vec{r}_{p1} - \vec{R}_i|) \quad (2-11a)$$

with

$$\phi_3(x) = c_3 e^{-\frac{1}{2} A_3 x^2},$$

$$\phi_4(x) = c_4 e^{-\frac{1}{2} A_4 x^2},$$

and

$$\mathcal{F} = \prod_{1 \leq i < j \leq N_3} f_{33}(r_{pi pj}) \prod_{N_3+1 \leq i < j \leq N} f_{44}(r_{pi pj}) \prod_{\substack{1 \leq i \leq N_3 \\ N_3+1 \leq j \leq N}} f_{34}(r_{pi pj}) \quad (2-11b)$$

with

$$f_{ab}(x) = e^{-K_{ab} v_{ab}(x)}$$

A_3 , A_4 , K_{33} , K_{44} and K_{34} are chosen as variational parameters.

K_{ab} 's measure the short-range repulsive interaction between the two atoms, which is electronic. Now that He^3 and He^4 atoms have the same electronic structure, the K_{ab} 's do not differ too much for all of the isotopic pairings.

We should keep in mind that the set of states $\{ \langle \vec{r}_i | p(c) \rangle \}$ represents the same physical state $|c\rangle$.

Lemma 1

Permuting particles on the sites which are held fixed is equivalent to permuting sites but fixing particle labels. (See Appendix B for proof).

Therefore, we can rewrite (2-11a) in the form

$$\phi_p = \prod_{i=1}^{N_3} \phi_3 (| \vec{r}_i - \vec{R}_{p1} |) \prod_{i=N_3+1}^N \phi_4 (| \vec{r}_i - \vec{R}_{p1} |) \quad (2-12)$$

Using the identity

$$\int_1 \cdots \int_N \phi_p \mathcal{F} \nabla_1^2 \phi_p \mathcal{F} = \frac{1}{2} \int_1 \cdots \int_N \phi_p^2 \mathcal{F}^2 \nabla_1^2 \ln(\phi_p \mathcal{F}) \quad (2-13)$$

we can separate E_0 into two parts

$$E_0 = E_{0b} + E_{mb} \quad (2-14)$$

where E_{0b} is a one-body part, and E_{mb} is a many-body part.

Actually

$$\begin{aligned}
 E_{Ob} &= \frac{\sum_p \int_1 \cdots \int_N \phi_p^2 \mathcal{F}^2 \left\{ -\frac{\hbar^2}{4m_i} \nabla_i^2 \ln(\phi_p \mathcal{F}) \right\} dr_1 \cdots dr_N}{\sum_p \int_1 \cdots \int_N \phi_p^2 \mathcal{F}^2 dr_1 \cdots dr_N} \\
 &= N [x t_3 + (1-x) t_4] \quad (2-15)
 \end{aligned}$$

where

$$t_3 = \frac{3\hbar^2 A_3}{4m_3} \quad \text{and} \quad t_4 = \frac{3\hbar^2 A_4}{4m_4} .$$

To treat the many-body part, we utilize the following mathematical technique

$$\begin{aligned}
 \sum_i \frac{1}{m_i} \nabla_i^2 \ln \mathcal{F} &= \sum_i \sum_{\substack{k \\ (k < i)}} \frac{1}{m_i} \nabla_i^2 \ln f_{ki} \\
 &+ \sum_i \sum_{\substack{\ell \\ (\ell > i)}} \frac{1}{m_i} \nabla_i^2 \ln f_{i\ell} \\
 &= \frac{1}{2} \sum_{i,j} \left(\frac{1}{m_i} + \frac{1}{m_j} \right) \nabla^2 \ln f_{ij}
 \end{aligned}$$

Defining

$$v_{ab}(r_{ij}) \equiv v_{ab}(r_{ij}) - \frac{\hbar^2}{2\mu_{ab}} \nabla^2 \ln f_{ab}(r_{ij})$$

with

$$\mu_{33} \equiv m_3, \quad \mu_{44} \equiv m_4 \quad \text{and} \quad \mu_{34}^{-1} \equiv m_3^{-1} + m_4^{-1},$$

we obtain

$$E_{mb} = \frac{1}{2} \frac{N_{33} + N_{44} + N_{34} + N_{43}}{D} \quad (2-16)$$

where

$$D = \sum_p \int_1 \cdots \int_N d\vec{r}_1 \cdots d\vec{r}_N \mathcal{F}^2 \phi_p^2 \quad (2-16a)$$

and

$$N_{ab} = \sum_{i,j} \sum_p \left\{ \cdots \int_N \mathcal{F}^2 \phi_p^2 \text{ (atom a for } r_i, \text{ b for } r_j) V_{ab}(r_{ij}) \right. \quad (2-16b)$$

First we shall rearrange the summation in a N_{ab} , say, N_{33} . Totally there are $N_3(N_3-1) N!$ terms in N_{33} : $N!$ from the summation $\sum_p$ and $N_3(N_3-1)$ from $\sum_{i,j}$ with both i and j being He^3 atoms. Now we split the summation $\sum_p$ into $\sum_{\mu, \nu} \sum_{P_{\mu\nu}}$. $P_{\mu\nu}$'s are those P-arrangements in which atoms i and j are fixed on the two sites μ and ν . So there are $(N-2)!$ terms in the sum $\sum_{P_{\mu\nu}}$. The total number of terms in $\sum_{\mu, \nu} \sum_{P_{\mu\nu}}$ is $N(N-1) \cdot (N-2)! = N!$ still. Further, we split the summation $\sum_{P_{\mu\nu}}$ into $\sum_{C_{\mu\nu}} \sum_{P(C_{\mu\nu})}$. $C_{\mu\nu}$'s are those C-arrangements in which atoms i and j are fixed on the two sites μ and ν . The relation between C-arrangements and P-arrangements has been discussed before: In a C-arrangement permuting identical particles does not generate a new arrangement. So, $\{P(C_{\mu\nu})\}$ forms a set of arrangements belonging to the same $C_{\mu\nu}$. There will be $(N_3-2)! N_4!$ terms in $\sum_{P(C_{\mu\nu})}$ and the total number of terms in $\sum_{C_{\mu\nu}} \sum_{P(C_{\mu\nu})}$ is

$$\frac{(N-2)!}{(N_3-2)! N_4!} \cdot (N_3-2)! N_4! = (N-2)! \quad \text{again.}$$

$$\therefore N_{33} = \sum_{i,j} \sum_{\mu,v} \sum_{c_{\mu v}} \sum_{p(c_{\mu v})} \int_1 \cdots \int_N \mathcal{F}^2 v_{33}(r_{ij}) \phi_{p(c_{\mu v})}^2(i-\mu, j-v) \quad (2-17)$$

Lemma 2 (See Appendix B for proof)

$$\begin{aligned} & \int_1 \cdots \int_N \mathcal{F}^2 v_{33}(r_{ij}) \phi_{p_1(c_{\mu v})}^2(i-\mu, j-v) \\ &= \int_1 \cdots \int_N \mathcal{F}^2 v_{33}(r_{k\ell}) \phi_{p_2(c_{\mu v})}^2(k-\mu, \ell-v) \end{aligned} \quad (2-18)$$

With the aid of Lemma 2, we can regroup the summations in N_{33} and obtain

$$\begin{aligned} N_{33} &= \sum_{\mu,v} \sum_{c_{\mu v}} \left\{ \sum_{i,j} \sum_{p(c_{\mu v})} \int_1 \cdots \int_N \mathcal{F}^2 v_{33}(r_{ij}) \phi_{p(c_{\mu v})}^2 \right\} \\ &= N_3! N_4! \sum_{\mu,v} \sum_{c_{\mu v}} \int_1 \cdots \int_N \mathcal{F}^2 v_{33}(r_{ij}) \phi_{p(c_{\mu v})}^2 \end{aligned} \quad (2-19)$$

or generally we have

$$N_{ab} = N_3! N_4! \sum_{\mu, \nu} \sum_{c_{\mu\nu}} \int_1 \cdots \int_N \mathcal{F}^2 v_{ab}(r_{ij}) \phi_p^2(c_{\mu\nu})$$

$$N_3! N_4! \sum_{\mu, \nu} \mathcal{N}_{ab} \quad (2-19b)$$

The number of terms in $\mathcal{N}_{33}$ is

$$\frac{(N-2)!}{(N_3-2)! N_4!}, \text{ in } \mathcal{N}_{44} \text{ is } \frac{(N-2)!}{(N_4-2)! N_3!}, \text{ and in}$$

$$\mathcal{N}_{34} \text{ is } \frac{(N-2)!}{(N_3-1)! (N_4-1)!}.$$

So the total number of terms in $\sum_{a,b} \mathcal{N}_{ab}$ is

$$\frac{(N-2)!}{(N_3-2)! N_4!} + \frac{(N-2)!}{(N_4-2)! N_3!} + 2 \frac{(N-2)!}{(N_3-1)! (N_4-1)!} = \frac{N!}{N_3! N_4!}$$

which is what we need.

For the denominator D in E_{mb} , we can write it in the original form $\sum_c \langle c | c \rangle$ instead of the later form (Eq. (2-16a)). Thus we have reduced the many-body part of the energy to

$$E_{mb} = \frac{1}{2} \sum_{\mu, \nu} \frac{\sum_{a,b} \sum_{c_{\mu\nu}} \int_1 \cdots \int_N \mathcal{F}^2 v_{ab}(r_{ij}) \phi_p^2(c_{\mu\nu})^{(i-\mu, j-\nu)}}{\sum_c \int_1 \cdots \int_N \mathcal{F}^2 \phi_p^2(c)}$$

(2-20)

In order to evaluate E_{mb} in Eq. (2-20), we shall apply the following approximation method. We call it the N_0 - body Approximation.

Consider a volume V surrounding the two sites μ and ν .
Let the total number of atoms inside V be N_0 . We require

$$N_0 \gg 1 \quad (2-21)$$

and

$$N_3 \gg N_0, \quad N_4 \gg N_0 \quad (2-22)$$

Then we approximate our integral within the summation $\sum_{c_{\mu\nu}}$
in the numerator of Eq. (2-20) by

$$(S_{c_{\mu\nu}}^{\text{out}}) (S_{c_{\mu\nu}}^{\text{in}}) \quad (2-23)$$

where

$$S_c^{\text{out}} \equiv \underbrace{\int \cdots \int}_{\text{outside } V} \mathcal{F}_{\text{out}}^2 \phi_{c_{\text{out}}}^2 \quad (2-23a)$$

and

$$S_c^{\text{in}} \equiv \underbrace{\int \cdots \int}_{\text{inside } V} \mathcal{F}_{\text{in}}^2 v_{ab}(r_{ij}) \phi_{c_{\text{in}}}^2(i-\mu, j-\nu) \quad (2-23b)$$

with

$$\phi_{c_{\text{out}}}^2 \cdot \phi_{c_{\text{in}}}^2 = \phi_{c_{\mu\nu}}^2$$

In the expression (2-23) we have taken $\prod_{\ell, m} f_{\ell m} \approx 1$ for particles ℓ inside V and particles m outside V . Since $f_{\ell m}$ measures the short-range correlation between the two particles ℓ and m , it is proper to put $f_{\ell m} = 1$ for all the particles ℓ and m , except those

nearby the boundary surface of V . The number of surface atoms is approximately $N_0^{2/3}$. If we further require

$$\frac{N_0}{N_0^{2/3}} = N_0^{1/3} \gg 1 \quad (2-24)$$

Our approximation (2-23) approaches an exact expression for the integral.

Let us, for simplicity, consider the term n_{33} in the numerator of Eq. (2-20). (n_{33} is defined by Eq. (2-19b)). Using the N_0 -body approximation,

$$n_{33} = \sum_{c_{\mu\nu}} (s_{c_{\mu\nu}}^{\text{out}}) (s_{c_{\mu\nu}}^{\text{in}})$$

Assuming for a particular arrangement $c_{\mu\nu}$, there are $M + 2$ He^3 atoms and $N_0 - M - 2$ He^4 atoms inside V . Sites μ and ν are occupied by two He^3 atoms. We may permute non-identical particles (but fixing the two He^3 atoms on sites μ and ν) to generate different $c_{\mu\nu}$'s. We may first hold both M and the arrangement inside V fixed, and vary the ways of arranging particles outside V . Secondly we hold M and the arrangement outside V fixed, and vary the configurations inside. Finally, we vary M .

Fixing M , the number of ways of varying arrangements outside V is

$$\Omega_M^{\text{out}} = \frac{(N - N_0)!}{(N_3 - N - 2)! (N_4 - N_0 + M + 2)!} \quad (2-25a)$$

Fixing M , the number of ways of varying arrangements inside V is

$$\Omega_M^{\text{in}} = C_M^{N_0-2} \quad (2-25b)$$

So we can break the summation $\sum_{C_{uv}}$ into

$$\sum_M \sum_{\text{out}} \sum_{\text{in}} \text{ or}$$

$$\mathcal{N}_{33} = \sum_{M=0}^{N_0-2} \sum_{\text{out}} (S_M^{\text{out}}) \sum_{\text{in}} (S_M^{\text{in}})$$

The summation $\sum_{\text{out}} (S_M^{\text{out}})$ is further replaced by $\Omega_M^{\text{out}} \langle S^{\text{out}} \rangle$, where $\langle S^{\text{out}} \rangle$ is the mean value of the integrals

$$\int \cdots \int \mathcal{F}_{\text{out}}^2 \phi_{\text{out}}^2$$

outside V

for different M 's. Since, by condition (2-22), we have $N-N_0 \gg M$, it is easy to see that this mean value $\langle S^{\text{out}} \rangle$ is independent of M , and our approximation

$$\sum_{\text{out}} (S_M^{\text{out}}) \approx \Omega_M^{\text{out}} \langle S^{\text{out}} \rangle \quad (2-26)$$

is nearly exact.

Noticing that

$$\frac{\Omega_M}{\Omega'} = \frac{(N-N_0)! \, N_3! \, N_4!}{(N_3-M-2)! \, (N_4-N_0+M+2)! \, N!}$$

(continued)

$$= \frac{N_3(N_3-1) \cdots (N_3-M-1) N_4(N_4-1) \cdots (N_4-N_0+M+3)}{N(N-1) \cdots (N-N_0+1)}$$

$$\begin{aligned} &\rightarrow \underbrace{xx \cdots x}_{M+2 \text{ in number}} \underbrace{(1-x)(1-x) \cdots (1-x)}_{N_0-M-2 \text{ in number}} \\ &= x^2 x^M (1-x)^{N_0-M} \end{aligned}$$

where $N_0^1 = N_0 - 2$, we have

$$\begin{aligned} n_{33} &= \Omega^1 x^2 \langle S^{\text{out}} \rangle \sum_{M=0}^{N_0^1} x^M (1-x)^{N_0^1-M} \sum_{\text{in}} (S_M^{\text{in}}) \\ &= \Omega^1 \langle S^{\text{out}} \rangle x^2 \underbrace{\int \cdots \int}_{N_0^1} dr_i \int dr_j \mathcal{F}_{\text{in}}^2 V_{33}(r_{ij}) \\ &\quad \prod_{\ell=1}^{N_0^1} \{ x \phi_3^2(\ell) + (1-x) \phi_4^2(\ell) \} \phi_3^2(i-\mu) \phi_3^2(j-\nu) \end{aligned}$$

We can apply the same technique to n_{44} , n_{34} and D , and obtain the following general expressions

$$\begin{aligned} n_{ab} &= \Omega^1 \langle S^{\text{out}} \rangle x_a x_b \underbrace{\int \cdots \int}_{N_0^1} dr_i \int dr_j \mathcal{F}_{\text{in}}^2 V_{ab}(r_{ij}) \\ &\quad \prod_{\ell=1}^{N_0^1} \{ x \phi_3^2(\ell) + (1-x) \phi_4^2(\ell) \} \phi_a^2(i-\mu) \phi_b^2(j-\nu) \end{aligned}$$

(2-27a)

and

$$D_{ab} = \Omega \langle S^{out} \rangle x_a x_b \underbrace{\int \cdots \int}_{N_0^p} dr_i \int dr_j \mathcal{Z}_{in}^2 \prod_{\ell=1}^{N_0^p} \{x \phi_3^2(\ell) + (1-x) \phi_4^2(\ell) \} \phi_a^2(i-\mu) \phi_b^2(j-\nu) \quad (2-27b)$$

Notice that we have classified D into D_{ab} 's according to our need. Substituting Eq. (2-27a) and Eq. (2-27b) into Eq. (2-20), we obtain the many-body energy E_{mb} . Further combining E_{mb} with Eq. (2-15) and Eq. (2-10), we obtain our final expression for the free energy

$$F = N [x t_3 + (1-x) t_4 + \frac{1}{2} x^2 W_{33} + \frac{1}{2} (1-x)^2 W_{44} + x(1-x) W_{34}] + NK T [-x \ln 2 + x \ln x + (1-x) \ln(1-x)] \quad (2-28)$$

where

$$W_{ab} = \frac{\underbrace{\int \cdots \int}_{N_0^p} dr_i \int dr_j \mathcal{Z}_{in}^2 v_{ab}(r_{ij}) \prod_{\ell=1}^{N_0^p} \{x \phi_3^2(\ell) + (1-x) \phi_4^2(\ell)\} \phi_a^2(i-\mu) \phi_b^2(j-\nu)}{\underbrace{\int \cdots \int}_{N_0^p} dr_i \int dr_j \mathcal{Z}_{in}^2 \prod_{\ell=1}^{N_0^p} \{x \phi_3^2(\ell) + (1-x) \phi_4^2(\ell)\} \phi_a^2(i-\mu) \phi_b^2(j-\nu)} \quad (2-28a)$$

By letting $N_0 = 2$ (the two atoms on sites μ and ν , interacting with each other through V_{ab}), we obtain the result for the two-body approximation: W_{ab} 's in Eq. (2-28) are now replaced by W_{ab} 's defined by

$$W_{ab} = \sum_{\nu} \frac{\int dr_i \int dr_j f_{ab}^2(r_{ij}) V_{ab}(r_{ij}) \phi_a^2(i-\mu) \phi_b^2(j-\nu)}{\int dr_i \int dr_j f_{ab}^2(r_{ij}) \phi_a^2(i-\mu) \phi_b^2(j-\nu)} \quad (2-28b)$$

Let us interpret our general result for the potential energies, i.e., Eq. (2-28a), in the following way. We expect a type-A atom sitting on site μ and a type-B atom sitting on site ν , interacting with one another through an effective potential V_{ab} . What do the surrounding atoms do? They contribute to the many body integral a product of single particle wavefunctions; each wavefunction is in the form of $x \phi_3^2 + (1-x) \phi_4^2$. So each surrounding atom acts as if it were composed of a fraction x of a He^3 atom and a fraction $1-x$ of a He^4 atom. We have thus obtained a result which satisfies us both intuitively and theoretically.

Chapter 3

Derivation of Free Energy Using

The Y-Ensemble

The N_0 -body approximation used in the course of our combinatorial analysis that leads to the solution of the ground state energy (described in the previous chapter) gives us an inspiration. We can work our thermodynamics within a restricted ensemble (we shall call it the Y-ensemble) of systems containing N_0 sites, taking the thermodynamic limit $N \rightarrow \infty$, $N_0 \rightarrow \infty$ and $\frac{N}{N_0} \rightarrow \infty$. The outside portion acts as a particle reservoir. The resulting expression of the free energy from the Y-ensemble method is not exactly the same as Eq. (2-28), due to the slightly different bases on which we work out the problem. In the two-body approximation, however, we obtain an identical expression from both approaches.

We still consider the lattice solid states $\{|m\rangle\}$. The thermodynamic properties of the system can be derived from the partition function

$$Z = \sum_m \langle m | e^{-\beta H} | m \rangle \quad (3-1)$$

Again, since $|m\rangle$ has translational symmetry of the lattice and does not localize the atoms, we shall consider the states $\{|n(c), c\rangle\}$. Each atom is localized around a lattice site in a state $|n(c), c\rangle$. It is conceivable to think these states $|n(c), c\rangle$ as phonon states.

The partition function can thus be replaced by

$$Z = \sum_c \sum_{n(c)} \langle n(c), c | e^{-\beta H} | n(c), c \rangle \quad (3-2)$$

The off-diagonal matrix elements of H , i.e., $\langle n'(c'), c' | H | n(c), c \rangle$, $(c \neq c')$, are expected to be at least three order of magnitude smaller than the diagonal elements, we can thus write

$$Z \approx \sum_c \sum_{n(c)} e^{-\beta} \langle n(c), c | H | n(c), c \rangle \quad (3-3)$$

The excitation part $\sum_{n(c)}$ in the total summation can be treated first, using Debye approximation

$$\sum_{n(c)} e^{-\beta} \langle n(c), c | H | n(c), c \rangle = e^{-\beta [E_0(c) + (\frac{T}{\theta_D(c)})^3 NKT]} \quad (3-4)$$

where $E_0(c)$ and $\theta_D(c)$ are the ground state energy and the effective Debye temperature respectively, for the arrangement c . Since we are interested in the temperature region $T \leq 0.5^\circ K$,

$$(\frac{T}{\theta_D(c)})^3 KT \sim (\frac{0.5}{20})^3 \cdot 0.5 \sim 10^{-5} \text{ } ^\circ K$$

which is negligible as compared to $E_0(c) \sim 0(1^\circ K)$. Therefore, we reduce our partition function (3-3) to approximately

$$Z \approx \sum_c \langle 0(c), c | e^{-\beta H} | 0(c), c \rangle \quad (3-5)$$

We shall work our problem (3-5) in a restricted ensemble that consists of systems $\{ S \}$ each of which is a part of the entire solid mixture. Every S contains a fixed number of lattice sites N_0 . Let $N_{1\uparrow}$, $N_{1\downarrow}$ and N_2 be the respective number of up-spin He^3 atoms, down-spin He^3 atoms, and He^4 atoms inside a system S . $N_{1\uparrow}$, $N_{1\downarrow}$ and N_2 can vary from one system to another, except $N_{1\uparrow} + N_{1\downarrow} + N_2 = N_0$ which is a fixed number. We require the following thermodynamic limit:

$$N_0 \gg 1 \quad (3-6)$$

$$N_3 \gg N_0, N_4 \gg N_0 \quad (3-7)$$

Also, we require none of N_3 and N_4 to be too small compared to N . For example, each one of N_3 and N_4 should be $\geq 10^{-5} N$, so they are still three orders larger than the maximum possible vacancy concentration. In this thermodynamic limit, our restricted ensemble (the Y-ensemble) is equivalent to the canonical ensemble (see Appendix A).

The partition function for our Y-ensemble is defined as

$$\mathcal{Z} = \sum_{N_{1\uparrow}=0}^{N_0} \sum_{N_{1\downarrow}}^{N_0-N_{1\uparrow}} \sum_c \langle c | e^{-\beta(H - \zeta N_1 - \zeta N_{1\downarrow})} | c \rangle \quad (3-8)$$

where we have shorthanded $| 0(c), c \rangle$ by $| c \rangle$. $\mathcal{Z}$ is the difference

in the He^3 and He^4 chemical potentials

$$\Sigma = \mu_3 - \mu_4 \quad (3-9)$$

We shall call

$$\sum_{N_{1\uparrow}=0}^{N_0} \sum_{N_{1\downarrow}}^{N_0-N_{1\uparrow}} \sum_c \langle c | \hat{O} | c \rangle \equiv \text{Tr } \hat{O} \quad (3-10)$$

Define a thermodynamic potential for the Y-ensemble:

$$Y = -KT \ln \mathcal{Z} \quad (3-11)$$

If we call the free energy of the canonical ensemble

$$Z = \sum_c \langle c | e^{-\beta H} | c \rangle \quad (3-12)$$

by F , or equivalently

$$F = -KT \ln Z \quad (3-13)$$

we have then

$$Y = F - \sum N_{1\uparrow} - \sum N_{1\downarrow} = F - \sum N_1 \quad (3-14)$$

($N_1 \equiv N_{1\uparrow} + N_{1\downarrow}$) . Now

$$\begin{aligned}
 dY &= -S dT - P dV + \mu_1 dN_1 + \mu_2 dN_2 - \sum dN_i - N_1 d\zeta \\
 &= -S dT - P dV + \mu_2 dN_0 - N_1 d\zeta
 \end{aligned} \quad (3-15)$$

$$\therefore Y = Y(T, V, N_0, \zeta) \quad (3-16)$$

This is ideal for our Y -ensemble in which N_0 is held fixed.

Defining the site occupation number

$$n_i = \begin{cases} 1, & \text{if there is an up-spin He}^3 \text{ on site } i \\ -1, & \text{if there is a down-spin He}^3 \text{ on site } i \\ 0, & \text{if there is a He}^4 \text{ on site } i \end{cases} \quad (3-17)$$

Thus $\text{Tr } \hat{O} = \sum_{\{n_i\}} \langle \{n_i\} | \hat{O} | \{n_i\} \rangle$. The total number of terms in the old summation is

$$\sum_{N_{1+}=0}^{N_0} \sum_{N_{1+}=0}^{N_0-N_{1+}} \sum_c (1) = \sum_{N_{1+}=0}^{N_0} \sum_{N_{1+}=0}^{N_0-N_{1+}} \frac{N_0!}{N_{1+}! N_{1+}! N_2!} = 3^{N_0} \quad (3-18)$$

which is also the number of terms in the new summation $\sum_{\{n_i\}}$. Now

$$N_1 = \sum_{i=1}^{N_0} |n_i| \quad (3-19)$$

$$H = H_0 + H_1$$

$$H_0 = \sum_{i=1}^{N_0} [t_3(i) |n_i| + t_4(i) (1 - |n_i|)] \quad (3-20)$$

$$H_1 = \sum_{i < j} \left[|n_i| |n_j| v_{33}(r_{ij}) + |n_i| (1 - |n_j|) v_{34}(r_{ij}) \right. \\ \left. + (1 - |n_i|) (1 - |n_j|) v_{44}(r_{ij}) \right] \quad (3-21)$$

where

$$t_3(i) = - \frac{\hbar^2}{2m_3} \nabla_i^2 \quad \text{and} \quad t_4(i) = - \frac{\hbar^2}{2m_4} \nabla_i^2 .$$

Introducing the density matrix

$$\rho = e^{-\beta(H - N_1)} / \mathcal{Z} \quad (3-22)$$

(3-11) becomes

$$Y = \text{Tr}(\rho H) + KT \text{Tr}(\rho \ln \rho) - \mathcal{Z} \text{Tr}(\rho N_1) + \lambda \text{Tr} \rho \quad (3-23)$$

To obtain a variational form of ρ , let us minimize Y with respect to ρ ,

$$\frac{\delta Y}{\delta \rho} = H + KT \ln \rho + KT - \mathcal{Z} N_1 + \lambda = 0$$

$$\therefore \rho = e^{-\beta(H - \mathcal{Z} N_1)} \quad (3-24)$$

Therefore, we take our trial density matrix in the form

$$\rho_t = \frac{1}{\mathcal{Z}_t} e^{-\beta(H_t - \mathcal{Z} N_1)} \quad (3-25)$$

with

$$H_t = \sum_{i=1}^{N_0} [\epsilon_1 |n_i| + \epsilon_0 (1 - |n_i|)] \quad (3-26)$$

and

$$\mathcal{Z}_t = \sum_{\{n_i\}} \frac{e^{-\beta \sum_{i=1}^{N_0} [\epsilon_1 |n_i| + \epsilon_0 (1 - |n_i|)] - \beta \sum_i |n_i|}}{\langle \{n_i\} | \{n_i\} \rangle}$$

$$= e^{-\beta N_0 \epsilon_0} [1 + 2 e^{-\beta(\Delta - \zeta)}]^{N_0} \quad (3-27)$$

where $\Delta \equiv \epsilon_1 - \epsilon_0$. The equilibrium He^3 concentration is

$$\langle |n_i| \rangle_t = \sum_{\{n_j\}} \frac{e^{-\beta N_0 \epsilon_0}}{\mathcal{Z}_t} |n_i| e^{-\beta \sum_{j=1}^{N_0} |n_j| (\Delta - \zeta)} \frac{\langle \{n_j\} | \{n_j\} \rangle}{\langle \{n_j\} | \{n_j\} \rangle}$$

$$= \frac{2e^{-\beta(\Delta - \zeta)}}{1 + 2e^{-\beta(\Delta - \zeta)}} \equiv x \quad (3-28)$$

which in the thermodynamic limit, approaches $\frac{N_3}{N}$. Also the He^4 concentration is

$$1 - x = \frac{1}{1 + 2e^{-\beta(\Delta - \zeta)}} \quad (3-29)$$

It is easy to derive the $-TS$ term in the free energy

$$KT \text{Tr}(\rho_t \ln \rho_t) = N_0 KT [-x \ln 2 + x \ln x + (1-x) \ln(1-x)] \quad (3-30)$$

Next let us calculate the energy terms,

$$\text{Tr}(\rho_t H) = \frac{e^{-8N_0\epsilon_0}}{\mathcal{Z}_t} \sum_{\{n_i\}} e^{-\beta \sum_{i=1}^{N_0} |n_i| \langle \Delta \rangle} \frac{\langle \{n_i\} | H | \{n_i\} \rangle}{\langle \{n_i\} | \{n_i\} \rangle} \quad (3-31)$$

Again as in Chapter 2, we choose our trial wavefunction $\langle \{\vec{r}_i\} | \{n_i\} \rangle$ for helium crystals as the product of single particle wavefunctions of the Gaussian type, times the product of two-body correlation functions of the Jastrow type:

$$\langle \{\vec{r}_i\} | \{n_i\} \rangle_{\text{trial}} = \left\{ \prod_{i=1}^N \phi_{n_i}(i) \right\} \mathcal{F} \quad (3-32)$$

where

$$\mathcal{F} = \prod_{1 \leq i < j \leq N_1} f_{33}(\vec{r}_{ij}) \prod_{\substack{1 \leq i \leq N_1 \\ N_1+1 \leq j \leq N_0}} f_{34}(r_{ij}) \prod_{N_1+1 \leq i < j \leq N_0} f_{44}(r_{ij})$$

with each $f_{ab}(x) \equiv e^{-K_{ab} v_{ab}(x)}$, and

$$\phi_0 (|\vec{r}_i - \vec{R}_j|) = C_4 e^{-\frac{1}{2} A_4 |\vec{r}_i - \vec{R}_j|^2}$$

$$\phi_{\pm 1} (|\vec{r}_i - \vec{R}_j|) = C_3 e^{-\frac{1}{2} A_3 |\vec{r}_i - \vec{R}_j|^2}$$

Again A_3 , A_4 , K_{33} , K_{34} and K_{44} are chosen as variational parameters. With this trial wavefunction (3-32), and using the identity

$$\int \mathcal{F} \prod_{i=1, i \neq l}^{N_0} \phi_{n_i}^2(1) \phi_{\alpha}(l) \nabla_l^2 (\phi_{\alpha}(l) \mathcal{F}) = \frac{1}{2} \int \prod_{i=1, i \neq l}^{N_0} \phi_{n_i}^2(1) \mathcal{F}^2 \phi_{\alpha}^2(l) \nabla_l^2 \ln \phi_{\alpha}(l) \mathcal{F} \quad (3-33)$$

also

$$\nabla_l^2 \ln [\phi_{\alpha}(l) \mathcal{F}] = -3 A_{\alpha} + \sum_j \nabla_l^2 \ln f_{lj} \quad (3-34)$$

We get

$$\text{Tr} (\rho_t H_0) = \text{Tr} (\rho_t H_0)_{\phi} + \text{Tr} (\rho_t H_0)_{\mathcal{F}}$$

$$\text{Tr} (\rho_t H_0)_{\phi} = N_0 (x \bar{t}_3 + (1-x) \bar{t}_4) \quad (3-35)$$

with

$$\bar{t}_3 \equiv \frac{3\hbar^2 A_3}{4m_3}, \quad \bar{t}_4 \equiv \frac{3\hbar^2 A_4}{4m_4}$$

$$\text{Tr}(\rho_t H_0) + \text{Tr}(\rho_t H_1)$$

$$= \sum_{i < j} \sum_{\{n_i\}} \frac{\int_1 \cdots \int_{N_0} \prod_{\ell=1}^{N_0} x_{n_\ell} \phi_{n_\ell}^2(\ell) v_{n_i n_j}(r_{ij})}{\int_1 \cdots \int_{N_0} \prod_{\ell=1}^{N_0} \phi_{n_\ell}^2(\ell)} \quad (3-35)$$

where

$$v_{n_i n_j}(r_{ij}) \equiv v_{n_i n_j}(r_{ij}) - \frac{\hbar^2}{2\mu_{n_i n_j}} \nabla^2 \ln f_{n_i n_j}(r_{ij}) \quad (3-37)$$

$$\mu_{0,\pm 1}^{-1} \equiv m_3^{-1} + m_4^{-1}, \quad \mu_{00} \equiv m_4, \quad \mu_{\pm 1, \pm 1} \equiv m_3$$

$$x_1 \equiv x, \quad x_0 \equiv 1-x$$

The second one of our resulting expressions (3-35) and (3-36) is slightly different from Eq. (2-28), the result derived through the combinatorial approach, unless in the two-body approximation (see Chapter 2 for details), that is, taking $\mathfrak{F} \sim f_{n_i n_j}(r_{ij})$ for each pair of atoms (n_i on site i , n_j on site j). Under this approximation, (3-36) becomes

$$\text{Tr}(\rho_t H_0) + \text{Tr}(\rho_t H_1) = N_0 \left(\frac{1}{2} x^2 \bar{w}_{33} + \frac{1}{2} (1-x)^2 \bar{w}_{44} + x(1-x) \bar{w}_{34} \right)$$

(3-38)

where again

$$\bar{w}_{ab} \equiv \frac{\int f_{ab}^2(r_{ij}) \phi_a^2(i) \phi_b^2(j) v_{ab}(r_{ij})}{\int f_{ab}^2(r_{ij}) \phi_a^2(i) \phi_b^2(j)}$$

which is identical to Eq. (2-28).

Our result for the Y-thermodynamic potential in the two-body approximation is then

$$\begin{aligned} Y_t = N \{ & x t_3 + (1-x) t_4 + \frac{1}{2} x^2 \bar{w}_{33} + \frac{1}{2} (1-x)^2 \bar{w}_{44} \\ & + x(1-x) \bar{w}_{34} + KT [-x \ln 2 + x \ln x + (1-x) \ln(1-x)] \} \\ & - N x \zeta \end{aligned} \quad (3-39)$$

Combining (3-39) with (3-14) we obtain our free energy F in the same expression as (2-28) with all of the w_{ab} 's replaced by $\bar{w}_{ab}$'s.

To estimate the correction term $Y - Y_t$, expand the Y-ensemble partition function $\mathcal{Z}$ knowing $\text{Tr} \rho_t (H - H_t) \ll \frac{1}{\beta}$:

$$\mathcal{Z} = \mathcal{Z}_t \left[1 - \beta \text{Tr } \rho_t (H - H_t) + \frac{\beta^2}{2} \text{Tr } \rho_t (H - H_t)^2 - \dots \right] \quad (3-40)$$

so

$$Y - Y_t = - \frac{\beta}{2} \left\{ \text{Tr } \rho_t (H - H_t)^2 - \left[\text{Tr } \rho_t (H - H_t) \right]^2 \right\} + \dots \quad (3-41)$$

which gives a tail part proportional to T^{-2} in the specific heat, as expected.

Chapter 4

Thermodynamics

The thermodynamics of the phase separation of helium solid mixtures is based upon Eq. (2-28).

$$F = N \left\{ x \bar{t}_3 + (1-x) \bar{t}_4 + \frac{1}{2} x^2 w_{33} + \frac{1}{2} (1-x)^2 w_{44} + x(1-x)w_{34} \right. \\ \left. + KT \left[-x \ln x - (1-x) \ln (1-x) \right] \right\} \quad (2-28)$$

Notice that the integrals $\bar{t}_3$, $\bar{t}_4$, w_{33} , w_{34} and w_{44} are functions of the He^3 concentration x . They depend also on the pressure P .

Keeping in mind that helium solids solidify at a pressure of over 25 atm, we should, therefore, consider the Gibbs free energy $G = F + PV$ instead of F , for the solid mixture.

Since Mullin, in his paper,⁶⁾ which we shall discuss in Chapter 5, derived an expression for the free energy identical to our expression (2-28), and since he computed numerically $\bar{t}_3$, $\bar{t}_4$, w_{33} , w_{34} and w_{44} at different He^3 concentrations, fixing $P = 35.8$ atm, we shall use his numerical results in our analysis.

$\bar{t}_3(x,p)$ and $\bar{t}_4(x,p)$ strongly depend on x , $v(x,p)$ is almost linear in x , the plots of these functions vs. x at $p = 35.8$ atm, are shown in Figure 2.

Following Mullin's approximate fitting of the kinetic energies and volume by convenient polynomial forms, we write

$$\bar{t}_3(x) = \bar{t}_3(1) + \beta (1-x) - \gamma x (1-x) \quad (4-1)$$

$$\bar{t}_4(x) = \bar{t}_4(0) - \mu x + \nu x^2 \quad (4-2)$$

$$P v(x) = P [x v(1) + (1-x) v(0)] - \sigma x(1-x) \quad (4-3)$$

The potential energies w_{33} , w_{34} and w_{44} are very weak functions of x . Rewriting the Gibbs free energy in the following form

$$\begin{aligned} G = & N \left\{ x \left(\bar{t}_3(x) + \frac{1}{2} w_{33} \right) + (1-x) \left(\bar{t}_4(x) + \frac{1}{2} w_{44} \right) \right. \\ & + x(1-x) \Delta w + KT [-x \ln 2 + x \ln x + (1-x) \ln (1-x)] \\ & \left. + P v(x) \right\} \quad (4-4) \end{aligned}$$

where $\Delta w \equiv w_{34} - \frac{1}{2} (w_{33} + w_{44})$, further combining (4-1), (4-2), (4-3) with (4-4), we have for the mixture

$$\begin{aligned} G = & N \left\{ x \left(\bar{t}_3(1) + \frac{1}{2} w_{33} \right) + (1-x) \left(\bar{t}_4(0) + \frac{1}{2} w_{44} \right) \right. \\ & \left. + x(1-x) [\Delta u - (\gamma - \nu) x] \right\} - T S_{\text{mix}} \quad (4-5) \end{aligned}$$

where $\Delta u \equiv \beta - \mu - \sigma + \Delta w$. The Gibbs free energy for the mixed phase relative to the Gibbs energy for the separated phases

$$\begin{aligned} G_{\text{sep}} = & N \left\{ x \left(\bar{t}_3(1) + \frac{1}{2} w_{33} \right) + (1-x) \left(\bar{t}_4(0) + \frac{1}{2} w_{44} \right) \right. \\ & \left. - KT [x \ln 2] \right\} \quad (4-6) \end{aligned}$$

is thus

$$G - G_{\text{sep}} = N \{ x(1-x) \Delta u - (\gamma - v) x + KT [x \ln x + (1-x) \ln (1-x)] \} \quad (4-7)$$

For helium solid mixtures at $P = 35.8$ atm, $\Delta u \sim 0.95^\circ\text{K}$ and $\gamma - v \sim 0.1^\circ\text{K}$. If $\Delta u > 0$, the solid mixture undergoes a phase separation at a finite temperature T determined by minimizing the Gibbs free energy relative to the separated phases, i.e.,

$$\frac{\partial(G - G_{\text{sep}})}{\partial x} = 0 \quad (4-8)$$

or

$$KT = \frac{(1-2x) \Delta u - x(2-3x)(\gamma-v)}{\ln \frac{1-x}{x}} \quad (4-9)$$

The energy $U(x)$ of a mixed phase, $-TS_{\text{mix}}$ term, and Gibbs free energies $G(x)$ and $G_{\text{sep}}(x)$ as functions of the He^3 concentration x are plotted in Figure 3. The T - x curve characterizing the phase separation is shown in Figure 4.

The critical temperature T_c can be found by taking

$$\frac{\partial^2(G - G_{\text{sep}})}{\partial x^2} = 0 \quad \text{and} \quad \frac{\partial^3(G - G_{\text{sep}})}{\partial x^3} = 0$$

Before continuing the analysis, let us digress for a moment to investigate how the free energy varies with the temperature. At

$T = 0$, the free energy is just the energy $U(x)$, which is always higher than the free energy of separated phases $G_{\text{sep}}(x)$, if $\Delta u > 0$. (We shall discuss the case when $\Delta u < 0$, later in this chapter). Therefore, if $\Delta u > 0$, the phase separation is complete at the zero temperature. As the temperature rises up, the entropy term $-TS$ pulls the $G(x)$ curve down (see Figure 3), and $G(x)$ shows two dips corresponding to x_1 and x_2 on the T - x curve (see Fig. 4). For $x < x_1$ or $x > x_2$ the complete mixing is favored. Further raising the temperature, until the critical temperature T_c is reached corresponds to a further lowering of the free energy until the two dips merge into one (see Fig. 5).

At this temperature we expect

$$\frac{\partial(G - G_{\text{sep}})}{\partial x} = 0 ,$$

$$\frac{\partial^2(G - G_{\text{sep}})}{\partial x^2} = 0 \quad (4-10)$$

and

$$\frac{\partial^3(G - G_{\text{sep}})}{\partial x^3} = 0 \quad (4-11)$$

Knowing that $\gamma - v$ is one order smaller than Δu , we obtain approximately the critical temperature

$$T_c \approx 0.5 \frac{\Delta u}{K} \quad (4-12)$$

at

$$x_c \approx \frac{1}{2} \quad (4-13)$$

So the T-x curve is approximately symmetrical with respect to $x = \frac{1}{2}$. However, since the non-vanishing term $(\gamma-v) x^2(1-x)$, or the contribution due to the difference in the partial compressibilities of He^3 and He^4 atoms, there is a skewness in the T-x curve, causing a slight shift in the critical temperature (see Fig. 4, x_c is shifted to the left from $x = \frac{1}{2}$). This phenomenon was first predicted by Mullin⁶⁾ upon the above reasoning, and later seen in the experiments.

As the temperature is increased further after passing the critical temperature, phase separation will never happen. Since the -TS term is proportional to T, it thus increases with temperature rapidly in its magnitude. While the energy U does not depend on T. The total Gibbs free energy is therefore lowered further (see Fig. 5). Now we can see the entire thermodynamics of a phase separation. Energy-wise separated phases are favored, since then the system is at a lower energy. But entropy-wise the mixed phase is favored, since the atoms are then more randomly distributed and therefore the entropy of the system is higher. So, at lower temperatures, the system favors separated phases because the entropy contribution is small (-TS small for low T). And at higher temperatures the system favors a mixed phase, for the -TS term becomes more and more important and overcomes the energy term.

Let us also discuss the situation for $\Delta u < 0$. In this case the energy $U(x)$ and Gibbs free energy $G(x)$ of a mixed phase is always lower than $G_{\text{sep}}(x)$ (see Fig. 6). Therefore, phase separation

cannot happen at any low temperatures. In fact, the atoms in the solid mixture attract each other to form a chemical compound.

As we have mentioned in Chapter 1, the nature of Δu determines whether a mixture system phase separates. Let us give some general discussion on Δu . Suppose the solid mixture is a classical one, by which we mean that the kinetic energy of the atoms is much smaller than the potential energy. If the interaction between the A-species atoms is different from that between the B-species atoms, we will have $\Delta w = w_{AB} - \frac{1}{2}(w_{AA} + w_{BB}) \neq 0$ and that dominates Δu . Remember these w 's are negative quantities. So $\Delta u \geq 0$ implies

$$|w_{AB}| \leq \frac{1}{2} (|w_{AA} + w_{BB}|) \quad (4-14)$$

Taking the upper sign in Eq. (4-14), i.e., the average of the like species interactions is more attractive than the interaction between the different species, we have phase separation. On the opposite, taking the lower sign in Eq. (4-14), i.e., the average of the like species interactions is less attractive than the interaction between the different species, we do not have phase separation, and the crystal forms a chemical compound, for example, NaCl.

In the case of an isotopic solid mixture where the interactions are the same between any two atoms, the difference in the kinetic energies of the two isotopes—however small it is—becomes important. This difference in the kinetic energies results in differences in

the atomic volumes v_A , v_B (of the pure phases) and v (of a mixed phase). Prigogine et.al.⁵⁾ argue that an isotopic solid mixture will ultimately phase separate as the temperature drops, due to the volume differences resulting from the kinetic energy difference. Phase separation in an isotopic solid mixture is a pure quantum effect. The argument provided by Prigogine et.al. is based on the facts

- (1) v_A , v_B and v are different (say $v_A > v > v_B$) due to the difference in the kinetic energies, and
- (2) Interactions between atoms are identical.

Whence they assume that the free energy of a mixed phase, for a given atomic volume and temperature, is the sum of the free energies of the two pure phases at the same atomic volume and temperature, minus $T S_{mix}$, i.e.,

$$F(v,T) = x_A F_A(v,T) + x_B F_B(v,T) - T S_{mix} \quad (4-15)$$

With this assumption, they are able to show the excess in the free energy (the difference in the free energies of a mixed phase and separated phases fixing T and P) to be

$$\Delta F = \frac{1}{2} x_A x_B (v_A - v_B)^2 (x_A F_A'' + x_B F_B'') > 0 \quad (4-16)$$

For a detailed analysis we refer the readers to Ref. (5).

Chapter 5.

Various Discussions5-1. Classical Theory

The traditional theory¹³⁾ for a classical binary solid mixture (A+B) starts with the assumption that atoms of both species are uniformly distributed throughout a certain lattice, so that the probability of finding an A-atom at any lattice site is $x \equiv \frac{N_A}{N}$, and that of finding a B-atom at any site is $1-x$. Since the atoms are very much localized, we can imagine they all sit at the bottoms of the potential wells (the lattice sites). The total potential energy of the solid mixture is then

$$P. E. = \sum_{i < j} v_{ij} (d_{ij}) \quad (5-1)$$

where d_{ij} is the distance between lattice sites i and j .

Consider a spherical shell the atoms on which have the same distance to the atoms at the center of the sphere. Let it be the α -th shell (α labels the shell), and let Z_α be the number of atoms on the shell. Let the center site be site i and the sites on the spherical shell be j . The probability that site i is occupied by an A-atom or a B-atom is x or $1-x$. Also, the probability that a j -site is occupied by an A-atom or a B-atom is x or $1-x$. So the total interaction between the atom on site i and the atoms on the shell (sites j) is

$$\begin{aligned}
 & x Z_{\alpha} x v_{AA}(d_{\alpha}) + x Z_{\alpha} (1-x) v_{AB}(d_{\alpha}) \\
 & + (1-x) Z_{\alpha} x v_{AB}(d_{\alpha}) + (1-x) Z_{\alpha} (1-x) v_{BB}(d_{\alpha}) \quad (5-2)
 \end{aligned}$$

The total potential energy of the crystal should be the summation of Eq. (5-2) over all shells α for center i , and over all sites i , that is,

$$\begin{aligned}
 & \frac{1}{2} \sum_i \sum_{\alpha} \{ \text{expression of Eq. (5-2)} \} \\
 & = \frac{1}{2} N \sum_{\alpha} \{ \text{expression of Eq. (5-2)} \} .
 \end{aligned}$$

The factor $\frac{1}{2}$ takes care of the double counting in the summation.

$$\begin{aligned}
 \therefore \text{P. E.} &= N \left\{ \frac{1}{2} x^2 \sum_{\alpha} Z_{\alpha} v_{AA}(d_{\alpha}) + \frac{1}{2} (1-x)^2 \sum_{\alpha} Z_{\alpha} v_{BB}(d_{\alpha}) \right. \\
 & \left. + x(1-x) \sum_{\alpha} Z_{\alpha} v_{AB}(d_{\alpha}) \right\} \quad (5-3)
 \end{aligned}$$

In the classical treatment the concept of zero-point motion does not exist, so at near-zero temperatures the total kinetic energy of the atoms is too small as compared with the total potential energy. Therefore, the total energy of the crystal is practically equal to the total potential energy, or (also by rearranging Eq. (5-3)).

$$U = N \left\{ x \frac{1}{2} \bar{v}_{AA} + (1-x) \frac{1}{2} \bar{v}_{BB} + x(1-x) \Delta \bar{v} \right\} \quad (5-4)$$

$$\text{where } \bar{v}_{AA} \equiv \sum_{\alpha} Z_{\alpha} v_{AA}(d_{\alpha}), \quad \bar{v}_{BB} \equiv \sum_{\alpha} Z_{\alpha} v_{BB}(d_{\alpha}),$$

$$\bar{v}_{AB} \equiv \sum_{\alpha} Z_{\alpha} v_{AB}(d_{\alpha}) \text{ and } \Delta \bar{v} \equiv \bar{v}_{AB} - \frac{1}{2} (\bar{v}_{AA} + \bar{v}_{BB}).$$

It is easy to see, the classical theory works well for those solid mixtures where the interactions are quite different between atoms belonging to the different species, and the atoms have large masses so that the kinetic energies are small. For isotopic solid mixtures the interactions are identical so that $\Delta \bar{v} = 0$ and the difference in the zero-point kinetic energies, however small it is, determines phase separation, as we have discussed in the previous chapter. In the case of quantum isotopic solid mixtures the zero-point kinetic energies of the atoms are large, and of course their difference determines the phase separation. But, the difference in the potential energies should not be as simple as $\Delta \bar{v} = 0$. The atoms move away from their lattice sites during the zero-point motion, and interact at different distances. Further, the kinetic energy due to the short-range correlation effects will contribute a part

$$\left(\sum_{i < j} - \frac{\hbar^2}{2\mu_{ij}} \nabla^2 \ln f_{ij} \right)$$

to the potential energy. Therefore, the net difference in the

effective potential energies is not zero, but some small quantity Δw (see Chapter 4).

The most important feature in the classical theory is the assumption that atoms are randomly distributed over the lattice. This assumption brings out a result, i.e., Eq. (5-4), which has a similar form as the result of our present theory, e.g. Eq. (2-28). However, we derive our result without using the assumption. This is an interesting point that we shall discuss in details in the next section where Mullin's theory is being examined. Mullin, in his theory, includes the zero-point kinetic energies but still keeps the same assumption that the classical theory is based on.

5-2. Mullin's Theory⁶⁾

Mullin's theory on the phase separation of helium solid mixtures was a progress in the sense that he has successfully calculated the T-x curve for the phase separation and predicted the existence of a skewness in the T-x curve.

We first outline Mullin's theory. He chooses a trial wavefunction, for the ground state of the mixtures, of the form

$$\psi_0 = \prod_i \phi_3(i) \prod_j \phi_4(j) \quad (5-5)$$

Then he evaluates the energy by a cluster expansion truncated after the two-body terms. The one-body energy term is given by

$$N [x_a \bar{t}_a + x_b \bar{t}_b] \quad (5-6)$$

where

$$\bar{t}_a \equiv \frac{3}{4} \frac{\hbar^2 A_a}{m_a} \quad \text{and} \quad \bar{t}_b \equiv \frac{3}{4} \frac{\hbar^2 A_b}{m_b} .$$

The two-body term associated with the interactions of (a,b) pairs is given by

$$x_a x_b N \bar{w}_{ab} = N x_a \sum_{R_{ij}} n_b(R_{ij}) \frac{\int \phi_a^2(i) \phi_b^2(j) f_{ab}^2(ij) V_{ab}(ij) d\vec{r}_i d\vec{r}_j}{\int \phi_a^2(i) \phi_b^2(j) f_{ab}^2(ij) d\vec{r}_i d\vec{r}_j} \quad (5-7)$$

where $V_{ab}(ij) = v(ij) - \frac{\hbar^2}{2\mu_{ab}} \nabla_i^2 \ln f_{ab}(ij)$, and $n_b(R_{ij})$ is the number of b-type particles in a shell a distance R_{ij} from a particle taken as origin. In order to relate $n_b(R_{ij})$ to the total number of particles on that shell $n(R_{ij})$ which is known, an assumption has to be made: " He^3 and He^4 particles are randomly distributed throughout a perfect bcc lattice." Thus there is no short-range order and

$$n_b(R_{ij}) = x_b n(R_{ij}) \quad (5-8)$$

then he writes the mixture ground state energy as

$$U = x t_3 + (1-x) t_4 + \frac{1}{2} x^2 \bar{w}_{33} + \frac{1}{2} (1-x)^2 \bar{w}_{44} + x(1-x) \bar{w}_{34} \quad (5-9)$$

The resulting equation (5-9) of Mullin's theory has the same form as our result Eq. (2-28) in the two-body approximation. However, Mullin's trial wavefunction ψ_0 of Eq. (5-5) does not describe a state completely. It is not known, on which sites the He^3 atoms are localized, nor on which sites the He^4 atoms are localized. As we know, having $\prod_i \phi_3(i)$ distributed on one part of the sites gives one energy for the system, and having $\prod_i \phi_3(i)$ distributed on another part of the sites gives another energy. Therefore, ψ_0 is not well defined. Further, as we know from our present theory, ψ_0 is not by any means an eigenstate of the Hamiltonian H .

Since ψ_0 is not well defined, the traditional assumption that the atoms are randomly distributed throughout a lattice becomes necessary in order to do the summation in the potential energy. In this respect Mullin's theory has made no improvement for the classical theory described in Section (5-1). In our present theory we are able to derive the energy without using this traditional assumption. We start with the set of states $\{|c\rangle\}$ each of which corresponds to the ψ_0 of Eq. (5-5) but is now well defined. The ground state is obtained by linearly superposing these states $|c\rangle$, and the ground state energy thus obtained has a naturally built-in concentration dependence. The resulting expression in our theory

not only describes the wavefunction on the two sites having interaction with each other, but also tells the nature of the wavefunction on every site besides those two sites. As expected intuitively, the wavefunction takes the form $x \phi_3^2 + (1-x) \phi_4^2$ on every site besides the two. In fact, our theory is a full many body theory. On the contrary, there exists a difficulty in Mullin's cluster expansion on working out the three body term.

5-3. Is Lattice Distortion Important?

The volume effects described in our context do not imply lattice distortion. Since the atoms move around the lattice extremely fast (frequency of exchanging sites $\geq 10^6/\text{sec}$, corresponding to a velocity of $\geq 10^{-2}\text{cm/sec}$), any locally distorted lattice may not last long enough, so that on an average in the time the effect in the lattice distortion may be small. Mullin,⁶⁾ in his paper, assumes the existence of permanent local distortions and thus estimates their effect based on his calculations. He finds that the critical temperature is lowered by this effect by only 0.02°K.

5-4. Summary and Prospects

In this theory we believe that we have solved the general problem of phase separation of a solid mixture, specifically helium solid mixture, based on first principles of the quantum mechanics. We have improved Mullin's theory in the very fundamental sense.

Experiments have shown that the exchange energy of the He^3

atoms in a helium solid mixture does not depend on the He^3 concentration strongly.¹⁴⁾ It is our prospect to construct a theory of calculating the exchange energy in the mixture phase, and to understand the weak concentration dependence of the exchange energy.

Also in the future we would like ^{to} investigate into a theoretically interesting problem whether a possible neutron-proton mixture in the neutron stars phase separates. A neutron and a proton have almost identical masses, so the difference in the kinetic energies must be small. The interactions between the nucleons are spin and iso-spin dependent, which makes the problem complicated. The exchange energies are high (just one order smaller than the diagonal elements) and cannot be neglected in the computation of the ground state energy. For the details of the nucleon solids, we refer the readers to Ref. (9).

Appendix A.

Equivalence of the Canonical Ensemble and the Y-Ensemble

The partition function for the Y-ensemble is

$$\mathcal{Z}(\alpha, V, T) = \sum_{N_1=0}^{N_0} \sum_{N_1=0}^{N_0-N_1} \alpha^{N_1} Z_{N_1}(V, T) \quad (\text{A-1})$$

where $\alpha \equiv e^{\beta \zeta}$, V is the volume for the N_0 atoms, and

$$Z_{N_1}(V, T) = e^{-\beta F(N_1, V, T)} \quad (\text{A-2})$$

is the partition function for the canonical ensemble. $v \equiv \frac{V}{N_0}$ is the atomic volume. Let us fix the temperature T throughout our discussions.

In the thermodynamic limit $N_0 \rightarrow \infty$ and $V \rightarrow \infty$, the free energy is proportional to V , or

$$F(N_1, V) = -\frac{1}{\beta} \ln Z_{N_1}(V) \equiv -\frac{V}{\beta} f(v) \quad (\text{A-3})$$

Thus

$$\mathcal{Z}(\alpha, V) = \sum_{N_1=0}^{N_0} \sum_{N_1=0}^{N_0-N_1} e^{V \phi(v, \alpha)} \quad (\text{A-4})$$

where

$$\phi(v, \alpha) \equiv f(v) + \frac{N_1}{V} \ln \alpha \quad (\text{A-5})$$

Now, $Z_{N_1}(V)$ vanishes whenever $N_1 > N_0(V)$. Further, it is clear that for large V ,

$$N_0(V) = a V \quad (A-6)$$

where a is a constant. Let the largest value among the terms in the polynomial of (A-4) be $e^{V\phi_0(\alpha)}$, where

$$\phi_0(\alpha) = \text{Max} \{ \phi(v, \alpha) \} \quad (A-7)$$

(corresponding to $N_1 = N_{10}$: $\phi_0(\alpha) = f(v_0) + \frac{N_{10}}{V} \ln \alpha$). Then the following inequality holds

$$e^{V\phi_0(\alpha)} \leq \mathcal{Z}(\alpha, V) \leq N_0^2(V) e^{V\phi_0(\alpha)} \quad (A-8)$$

Using (A-6) we obtain

$$e^{V\phi_0(\alpha)} \leq \mathcal{Z}(\alpha, V) \leq (a V)^2 e^{V\phi_0(\alpha)}$$

or

$$\phi_0(\alpha) \leq \frac{1}{V} \ln \mathcal{Z}(\alpha, V) \leq \phi_0(\alpha) + \frac{2 \ln(a V)}{V} \quad (A-9)$$

Therefore,

$$\lim_{V \rightarrow \infty} \frac{1}{V} \ln \mathcal{Z}(\alpha, V) = \phi_0(\alpha) \quad (A-10)$$

This shows that

$$\mathcal{Z}(\alpha, V) \approx e^{-B(F - \sum N_{10})} \quad (A-11)$$

So the Y -ensemble is equivalent to the canonical ensemble.

Appendix B
Proof of the Lemmas

Lemma 1

Permuting particles on the sites which are held fixed is equivalent to permuting sites but fixing particle labels.

Proof: Let $pi = \ell$ in Eq. (2-11A). Then $i = p^{-1}\ell$. Also let $pj = m$ in Eq. (2-11B). We can write

$$\begin{aligned} \langle \{\vec{r}_i\} | p \rangle &= \prod_{\ell \in N_3} \phi_3 (|\vec{r}_\ell - \vec{R}_{p^{-1}\ell}|) \prod_{\ell \in N_4} \phi_4 (|\vec{r}_\ell - \vec{R}_{p^{-1}\ell}|) \\ &\quad \prod_{\ell, m \in N_3} f_{33} (|\vec{r}_{\ell m}|) \prod_{\ell, m \in N_4} f_{44} (r_{\ell m}) \prod_{\substack{\ell \in N_3 \\ m \in N_4}} f_{34} (r_{\ell m}) \end{aligned} \quad (B-1)$$

Since the sets $\{p\}$ and $\{p^{-1}\}$ are equal, $\langle \{\vec{r}_i\} | p \rangle$ in Eq. (B-1) thus becomes a wave-function in which the sites are permuted.

Lemma 2

Verify Eq. (2-18).

Proof: Let us define $p_i (c_{\mu\nu})$ as

$$\begin{aligned} r_m \text{ on } R_\mu, \quad r_i \text{ on } R_\mu, \quad r_j \text{ on } R_\nu, \quad r_k \text{ on } R_\lambda, \quad r_\ell \text{ on } R_\sigma \\ (m \neq i, j, k, \ell). \end{aligned}$$

And define $p_2(c_{\mu\nu})$ as

$$r_m \text{ on } R_m, r_i \text{ on } R_\lambda, r_j \text{ on } R_\sigma, r_k \text{ on } R_\mu, r_\ell \text{ on } R_\nu \\ (m \neq i, j, k, \ell).$$

Then

$$\int_1 \cdots \int_N \mathcal{F}^2 v_{33}(r_{ij}) \phi_{p_1}(c_{\mu\nu}) (i-\mu, j-\nu) \\ = \int_1 \cdots \int_N \prod_{p < q} f^2(r_{pq}) v_{33}(r_{ij}) \prod_m \phi_m^2(|\vec{r}_m - \vec{R}_m|) \phi_3^2(|\vec{r}_i - \vec{R}_\mu|) \\ \phi_3^2(|\vec{r}_j - \vec{R}_\nu|) \phi_3^2(|\vec{r}_k - \vec{R}_\lambda|) \phi_3^2(|\vec{r}_\ell - \vec{R}_\sigma|) \quad (B-2)$$

Relabeling $\vec{r}_i$ by $\vec{r}_k$ and $\vec{r}_j$ by $\vec{r}_\ell$, we transform (B-2) into

$$\int_1 \cdots \int_N \prod_{p < q} f^2(r_{pq}) v_{33}(r_{k\ell}) \prod_m \phi_m^2(|\vec{r}_m - \vec{R}_m|) \phi_3^2(|\vec{r}_k - \vec{R}_\mu|) \\ \phi_3^2(|\vec{r}_\ell - \vec{R}_\nu|) \phi_3^2(|\vec{r}_i - \vec{R}_\lambda|) \phi_3^2(|\vec{r}_j - \vec{R}_\sigma|) \\ = \int_1 \cdots \int_N v_{33}(r_{k\ell}) \phi_{p_2}(c_{\mu\nu}) (k-\mu, \ell-\nu) \mathcal{F}^2 \quad (B-3)$$

Q.E.D.

Figure 1. A particular arrangement C of the atoms. Black and white circles represent He^4 and He^3 atoms respectively.

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Figure 2. Upper curve is plot of mixture volume $v(x)$ vs. He^3 concentration x . Curve $\Delta \bar{t}_3$ is a plot of the difference between He^3 kinetic energy in the mixture and in the pure state ($t_3(x) - t_3(1)$) at constant $P = 35.8$ atm. $\Delta \bar{t}_4$ is a similar curve for He^4 .

Figure 3. $U(x)$, $G_{sep}(x)$, $G(x)$, and $-TS_{mix}$ vs. He³ concentration x , for $\Delta u > 0$.

Figure 4. Theoretical phase-separation curve for $P = 35.8$ atm.

Figure 5. $G(x, T = T_c)$ and $G(x, T > T_c)$ vs. He^3 concentration x .

Figure 6. $U(x)$, $G(x)$ and $G_{\text{sep}}(x)$ vs. He^3 concentration x , for $\Delta u < 0$.

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