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Computations in Statistical Mechanics

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COMPUTATIONS IN STATISTICAL MECHANICS

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In this series of lectures, I would like to give a survey of the enormous impact that numerical calculations have had in the field of statistical mechanics or, in other words, in the solution of the many-body problem. These calculations were made possible only through the availability of high speed digital computers and through the development of new numerical techniques uniquely suited to these computers. By these means some of the mathematical difficulties which had prevented progress in the field could be circumvented and new physical insight into the behavior of many interacting particle systems were gained.

The purpose of these talks is to outline the numerical procedures without going into either excessive technical details on the computational procedures or the rigorous mathematical proofs justifying the methods used. These can be found in the references applied. Similarly, the number of physical situations to which these numerical methods have been applied have rapidly multiplied in recent years, so that only the highlights can be presented. The topics are selected primarily on the basis of their fundamental contributions to the understanding of interesting physical phenomena and the validity of various mathematical methods to describe them, with examples chosen chiefly from my own work. Further illustrations

and more detail can again be found in the references, although that list is not intended, by any means, to be exhaustive. The intent of the lectures is to give a flavor of the contribution these numerical methods can make to statistical physics by discussing in a general way some outstanding examples.

I. GENERAL CONSIDERATIONS

Statistical mechanics is a suitable field in which to apply numerical techniques because the physics has been well established for many decades and the difficulties that are faced are of a mathematical nature. These difficulties are basically due to our inability to deal with multidimensional mathematical objects, whether they are integrals, differential equations, Green's functions or what have you. To be sure, the partition function, which is the basic multidimensional quantity to be evaluated in equilibrium statistical mechanics, can be determined in a few simple situations, such as for the perfect gas and the harmonic crystal; however, in each of these cases, the problem can be rigorously reduced to a product of one dimensional problems. Furthermore, much of the interesting physics is lost in these models.

For more realistic cases, because of the mathematical difficulties, the problem must be approximated by reducing the dimensionality of the system to low order. Most of the often used statistical mechanical theories, in fact, reduce the complex physical situation to a one particle problem, where the rest of the particles in the system merely provide an

average (mean) field with which the one particle interacts. Examples of these are the van der Waals model for the thermodynamic properties and the Langevin model of Brownian motion. Another class of one particle theories might be called self-consistent models, such as the Wigner-Seitz model for a solid, the Lennard-Jones Devonshire model of a liquid, or the Hartree-Fock solution of an atom. If these models are only slightly extended to deal with two independent particles, such as in the pair product simplification used in the superposition approximation to describe fluids and the Jastrow wave function approximation to describe quantum mechanical systems, one is already faced with a formidable mathematical problem generally requiring numerical techniques for its solution.

The computer, to be sure, also can not evaluate an Avogadro number dimensional mathematical equation, which typically is required. On the other hand, the computer can be made to simulate the behavior of a many-body problem involving a few hundred particles as accurately as is required from a physical point of view. Moreover, as shall be seen, the difference between dealing with a few particle approximation as required analytically, and a few hundred particle approximation as is possible numerically is the difference between a generally poor approximation and one that almost all the time represents the properties of a macroscopic system very well.

One of the outstanding exceptions is in phase transition regions where fluctuations are large, involving more than a few hundred particles. In that case, the computer results are distorted as well, however, not so seriously that one cannot reproduce some of the analytically known results

of the phase transition in the Ising model, for example. To be sure the Ising model itself represents a drastic reduction in the number of variables (degrees of freedom) with which to describe a phase transition, since the analytical solution is restricted to a two-dimensional system, the spins are confined to lattice sites and can only assume two possible values, and there must be an equal number of each type. A measure of the analytical difficulties for even this restricted problem is that it has not yet been solved in three dimensions in spite of many tries by outstanding scientists.

(A) Limitations:

In fact, all the limitations of the numerical method are connected with the inability to deal with very large sized systems and to simulate their behavior for very long times. This is basically due to the finite memory size and limited speed of basic operations on even the fastest and biggest computers available. This situation is not likely to significantly change in the foreseeable future with even more advanced computers.

The problem can perhaps best be illustrated by considering the length of time for which it is possible to follow a system of particles by the numerical method called molecular dynamics. In molecular dynamics, the classical Newtonian equations of motion of several hundred particles, all interacting simultaneously, are solved by brute force numerically by advancing the positions of the particles a small time step during which the forces on each particle can be assumed to be constant. The efficiency with which even the most advanced computer can do these time steps, however, is many orders of magnitude slower than in a real system. Thus, during a run of 10 hours on such a computer, the motion of the particles in a real liquid have

been followed for only 10^{-9} sec. This precludes using this method for following rate processes having longer relaxation times than that time.

One would have thought that this would make it impossible to study any hydrodynamic phenomena since they were believed to occur on a very long time scale for macroscopically large systems. As will be seen, certain transport phenomena that were studied on computers could be identified with hydrodynamic motion occurring on a microscopic scale. Yet, the computers were limited in following this hydrodynamic motion for very long; not because, in this case, of time limitations but because the finiteness of the system caused boundary interference effects to occur. In general, to minimize boundary effects, periodic boundary conditions are imposed, but even these distort the results from infinite systems. Serious effects of boundaries are frequently investigated by studying a property for several different numbers of particles.

(B) Advantages

Another serious limitation of numerical solutions is that, like an experiment, only a specific solution for a given set of conditions is obtained. Like experiments, they can sometimes be synthesized into a general solution, which could only be recognized by having a few specific examples worked out. More frequently, a general asymptotic solution can be recognized as valid only under more restricted conditions. Most frequently approximate models can be tested for their validity and if found wanting, better approximations can be suggested which summarize the specific results. In these respects, the numerical results are often more helpful than experiments, because they can be designed for more mathematically tractable situations. Furthermore, they can

give more detail than is easily experimentally accessible. For example, the potential of interaction between the particles can be made strictly pairwise additive and of a particularly simple form, such as a hard sphere potential. For such a system, the Boltzmann H-function or the triplet spacial distribution function can be evaluated to test previous hypothesis about their behavior. These are examples of functions which have not been experimentally measurable, but whose characteristic has been essential to the theoretical understanding of many particle systems. Not only is it numerically easy to evaluate these quantities, but it is possible to evaluate them over a much wider range of conditions, such as density and temperature, than can usually be covered by experiments.

The computer can out-perform experiments because it has a better resolution for small distances and short times. Most of our experimental tools have great difficulty observing phenomena at either a distance scale of the size of an atom or at the time scale of the time between collisions of two particles in a dense fluid, and that is just the scale at which the computer simulation operates. For larger distances and larger times, as pointed out before, the computer simulation fails. Since most of the statistical mechanical effects occur at the microscopic distance and time scale, the computer results have provided powerful insight into the mathematical structure of the many-body equations. By removing the restriction to tractable mathematics, it has become possible to investigate what essential physical processes dominate various phenomena. With the advantages of higher resolution than experiment it has even been possible to discover previously unsuspected physical processes.

II. NUMERICAL METHODS

There are two basic numerical procedures that have been developed for statistical mechanical investigations which would have been impossible to implement without fast digital computers. One of these has already been mentioned; molecular dynamics.¹ With that method it is possible to follow a system of particles to equilibrium and, for example, study how the Boltzmann H-function decays. In order to obtain the average behavior of the H-function, it is necessary to run a large number of systems from a series of initial states all of which are consistent with some sort of constraint. For example, for the H-function the constraint might be uniform spacial distribution of the particles (at lattice positions) over the available space but with a non-equilibrium velocity distribution such that each particle has the same speed but in a random direction.

Once the system has reached equilibrium, it is possible to determine the thermodynamic properties by taking time averages, for example, of the average kinetic and potential energy from which the temperature and the internal energy can be obtained. By this procedure, the whole apparatus of equilibrium statistical mechanics, that is the ergodic hypothesis, is bypassed. Once equilibrium is reached, it is however also possible to determine transport properties. This is done by studying the fluctuations about equilibrium, that is the transport coefficients are determined by the rate at which various fluctuations decay or dissipate.² Another possible way that has recently been pursued to determine transport coefficients is to set up a steady state for the particles in the presence of an appropriate external field, analogous to how such transport coefficients are traditionally experimentally determined.³

The other numerical method, misnamed the Monte Carlo method, utilizes the apparatus of equilibrium statistical mechanics and, hence, can only determine thermodynamic properties.⁴ By comparing the results of these two different numerical procedures for identical systems for some thermodynamic property, it has been possible to get a specific instance for the validity of the ergodic hypothesis. Needless to say, the time averaged property obtained by molecular dynamics has, in the many instances that it has been checked, agreed within statistical accuracy of the result with the phase space average determined by the Monte Carlo method.

Ironically, the two numerical procedures are generally indistinguishable in terms of the amount of computer time required to obtain equilibrium properties to a given accuracy. Thus, from a numerical point of view, the formulation of phase space averaging seems unnecessary, although in some more complex situations the Monte Carlo method does have some advantage in computational efficiency. One further advantage of the Monte Carlo method should be mentioned in this connection. The molecular dynamics method is necessarily restricted to microcanonical ensemble averages due to conservation of total energy in the calculation. The Monte Carlo method, on the other hand, is much more versatile in this respect, although it is not always clear which ensemble is better in any given situation.

(A) Random Processes

A truly random (Monte Carlo) method by which to evaluate the multi-dimensional integral of the partition function is not practical.⁵ The difficulty is that the partition function is a highly dimensional integral of a sharply peaked function; namely, the exponential of the potential energy of the system. The potential energy of the system for most of the

a priori possible configurations of the molecules in the system is very large compared to those near the more probable configurations, namely those near the potential energy minimum. Thus, out of the total number of possible arrangements of molecules, only a very small fraction make any significant contribution to the integral, which is merely another way of saying the integrand is highly peaked. The Monte Carlo evaluation of a highly dimensional integral is difficult enough, but a highly peaked one presents further serious problems.

(a) Multidimensional Integration

Monte Carlo evaluation of integrals involves placing random points in the space over which the integral is to be performed, in this case it would be the volume of the system, which, since it is supposed to be infinite, presents another difficulty. For each point that is placed into the space it is ascertained whether it is under the function or outside the function. With a sufficient number of such random placing of points in this space, it is possible to determine the area under the integral since it is the fraction of the points under the function times the known total volume of the space. The assumption is that a sufficient number of Monte Carlo placements have been made to uniformly cover the available space. The accuracy with which the integral has been determined depends not only on that but also, on what might be loosely called the smoothness of the function. The density of Monte Carlo points must be so large that the average distance between these points is small compared to the narrowest region of the integrand, otherwise that region would be poorly estimated. Thus, a highly peaked function in a large space requires a very large number of Monte Carlo points. Ways to overcome that difficulty are by mathematical transformations that lead

to a smoother integrand in a more limited space.

Even if that were possible, the high dimensionality would still make the problem virtually impossible, since to cover such a space even sparsely with points exceeds the limitation of computers. This can be seen from the example of covering only a ten-dimensional space with only 10 points in each dimension. The 10^{10} operations necessary, each requiring typically a minimum of 10^{-6} sec., make this problem consume one hour of machine time, without even considering the time consuming task of determining where the points fall. For this reason, practical Monte Carlo evaluation of multidimensional integrals with any accuracy is confined to less than 20 dimensions. A practical statistical mechanical application of this procedure can be found in the evaluation of higher virial coefficients.⁶ Beyond the fourth virial coefficient analytical methods generally fail, even for simple model potentials, and hence the above numerical procedure can be used to evaluate a few higher ones. Beyond the eighth or so virial coefficient, the numerical procedure for the above stated reasons becomes time consuming because of the high dimensionality.

(b) Ensemble

Another form of the Monte Carlo scheme, which was actually tried, points out the same difficulty in a more physical way. Suppose you want to make up one member of an ensemble at a given number density, N/V , by randomly placing N molecules in a volume, V . After having done that, one would calculate the total potential energy of that system and according to the principles of statistical mechanics, that particular configuration would be given a probability or weight of the exponential of that potential divided by kT , that is

the Boltzmann factor, where k is Boltzmann's constant and T is the given temperature. The temperature, together with the density, define the thermodynamic state of the system. This process is repeated many times to make up many members of the ensemble so that thermodynamic averages can be determined.

The difficulty with this procedure is that with overwhelming probability, a very improbable configuration of the system is selected, that is one of very high potential energy. For example, if the pair interaction potential were chosen to be that corresponding to hard spheres, almost all configurations at any but very low density would be such that some hard spheres would overlap. By overlapping is meant that the center of two hard spheres would be closer than the diameter of the hard sphere. Thus, overlapping spheres have infinite potential energy and hence the configuration has zero probability. The reason for the high probability of overlap in a randomly chosen configuration is that even in a dense gas the spheres have a somewhat ordered configuration. The higher the density, the more it is necessary to order the spheres so that they can be packed into the given volume. The greater the order of the configuration is, the less likely it will be generated from a random selection of positions.

(c) Wrong Ensemble

To overcome this difficulty, one might have thought one could place the particles into the volume one at a time.⁷ Thus, a sphere would be placed randomly into the volume only if that sphere did not overlap with any of the spheres previously placed. If it did overlap, it would be rejected and another tried. This procedure to build up a member of an ensemble has two serious flaws. One is a practical one, namely, it is still not possible

to reach very high density. At a density approximately corresponding to the one where a real system would be at its critical density, it is no longer possible to place another particle into the system, that is, virtually every placement is rejected. This is again because random placements lead to inefficient packing with large spaces between the spheres which cannot accomodate another sphere after a rather low density is exceeded.

The other flaw is a fundamental one, namely the method does not select a proper member of an ensemble. The only statistical mechanically sound procedure is to select all the positions at one time from a set of random numbers, as was first suggested, and then reject or accept the configuration of spheres according to whether there are any overlaps. The procedure of putting the spheres in one at a time selects a set among the random numbers which leads to wrong weighting of the members of an ensemble. Perhaps the simplest way to illustrate that is to show that for three hard spheres the probability of obtaining a given final configuration is different if they are placed in one at a time depending on the order in which they are placed, thus invalidating the procedure. The probability of placing a sphere into the volume is proportional to the volume accessible. As a consequence, if the final configuration of the three spheres is such that two of them are so close that a third sphere cannot be placed between them, then the probability of placing a third one far away from these two is different than if that third one had been accepted first and one of the close in ones last.

(B) Monte Carlo Method

Since the random procedures fail, it is necessary to go to the next order of stochastic complexity to evaluate statistical mechanical averages,

and that is by means of a random walk in configuration space.⁸ That random walk generates a Markov chain in which each state depends only on the previous state. Furthermore, the transition probability between two successive states must be such that averages over all the states developed in the Markov chain correspond to an ensemble average. The problem is to determine these transition probabilities to achieve this aim, namely the one that each state generated recurs with a frequency corresponding to its Boltzmann weighting. If configurations could be preselected with Boltzmann probability, then Boltzmann averages can be obtained by weighting all the generated configurations equally. This process corresponds to importance sampling where only configurations near the energy minimum are generated thus eliminating the wasteful procedure in random sampling where many improbable configurations have to be discarded.

The transition probability is not hard to find as illustrated for a dense system of hard spheres. A number of spheres are initially placed into the volume in any non-overlapping configuration, usually lattice positions, according to the density to be investigated. Next, a sphere is selected randomly and displaced by a random amount in a random direction. The size of the displacement is in principle irrelevant; however, in practice it determines the rate at which the system wanders through phase space. This is easily visualized since too small displacements leave the system little changed for many such displacements, while too large displacements have the same effect since the displacements are rejected. This is because after an attempted random displacement of a randomly chosen particle, the displacement is only accepted if it does not lead to an overlap with any sphere in the system. If it does not lead to overlap, another member

of the Markov chain has been generated. If overlapping results, the move is rejected, and the particle replaced, and the old configuration must be counted again in any averaging procedure over the Markov chain. The latter requirement must be imposed so that the system satisfies microscopic reversibility. More loosely speaking, the configuration must be recounted because the rejection of the move indicates the higher probability of the original configuration.

(a) Ergodicity

A succession of such random displacements of randomly chosen particles then constitutes a random walk in phase space. The only other requirement on the transition probability besides microscopic reversibility, and the trivial one that the probability is normalized, is that it is possible to go from any accessible state to any other by a series of finite one particle displacements; that is, that the system is ergodic. That has more to do with the choice of the initial state of the system and the number of attempted moves, than with the choice of the form of the transition probability. One defines a system as being ergodic and in the same class if by a series of single moves one can reach any state of the system independent of the initial state.⁹

In proving ergodicity for the Markov chain under consideration, one can take advantage of the fact that on the computer one is necessarily dealing with a finite chain, because the position of the particles can only be specified in a discreet space since there is an upper limit to the significant numbers by which the positions of particles can be specified. Hence, the Markov chain is necessarily ergodic in the sense that there is a mean finite recurrence time for each state in the same class. More troublesome is whether the finite time is sufficiently short in terms of the number of moves required, so that reasonable computer runs can cover phase space sufficiently well. There is

no theoretical guidance on this point and usually no difficulty is encountered as judged empirically by averages over runs of varying length.

Some practical difficulties are, however, encountered, as will be seen, when there are two separate or nearly separate regions in phase space. If there are separate regions in phase space then only averages over each class of such states is possible and the class is entirely determined by the choice of initial states. An example is the glassy and crystalline state of hard spheres at high density. It is possible to so jam up a finite number of hard spheres in a given volume that there is no way to rearrange them into the thermodynamically more stable crystalline state. This is a situation where for a finite system configuration space has been separated into two classes. For an infinite system, there is always an improbably large density fluctuation which will allow the glass to rearrange itself into the crystalline form. In that case the two classes of configuration in phase space are connected by a narrow passage, reflecting the improbability of that event. Thus, one has to face the problem that for finite systems phase space can be distorted and that rigorous proofs of ergodicity for such systems are likely to be confined to a given class.¹⁰

A case where different classes of phase space are connected by a narrow passage occurs also for hard spheres in the fluid-solid phase transition region; the two classes corresponding to the fluid and solid pockets. As will be seen, the finite system jumps sufficiently rarely from one pocket to the other that it has not been possible at some densities to get a meaningful average over both pockets for even the longest computer runs on the fastest machine available. As a consequence, the average over each pocket has to be given separately as if the thermodynamic functions at these densities were two valued.

(b) General Procedure

The impression that these problems only occur for hard sphere systems should be dispelled. For a more realistic interaction potential between a pair of particles, the repulsive forces still predominate at sufficiently high density leading to similar difficulties. For such a realistic potential the random walk procedure must be slightly modified. This time a random displacement of a randomly chosen particle is allowed with Boltzmann probability by evaluating the energy change resulting from the move. The move is allowed with probability of the exponential of this energy change divided by kT . This is technically achieved by comparing a random number with that exponential. If the random number is less than the exponential, the move is allowed, if not, the move is disallowed and the configuration obtained by replacing the particle at its original position is counted again in the statistical mechanical averaging.

Starting from some arbitrarily chosen initial configuration, most moves initially will be allowed as the system moves towards its energy minimum. After the system is near that state, it moves away from that minimum only with Boltzmann probability. It is only then that the averaging procedure is instituted; the early part, as the system moves toward equilibrium, being discarded. This initial phase is usually over very quickly. After equilibrium is reached, some unfavorable moves must be allowed, otherwise eventually the system would get frozen into its lowest potential energy state; that is all possible moves would increase the potential energy. Under those circumstances it is no longer possible to take averages.

(C) Molecular Dynamics

In comparison to the Monte Carlo method, the molecular dynamic method

is completely deterministic.¹¹ The particles are given positions and velocities and the equations of motion are followed. This can be done more accurately and faster if the potential of interaction is chosen to be of the hard sphere or square-well type. For such potentials, the only forces are impulsive ones at the discontinuities. The system of simultaneous differential equations then reduces to a system of simultaneous algebraic equations which can be solved for the time to the next collision among all the set of particles. Proceeding collision by collision the time evolution of the system is obtained. There are some obvious technical arrangements of the calculation that make this procedure efficient when a large number of particles are followed. In the Monte Carlo calculation, as well as in molecular dynamics, the calculation can be arranged such that in a given amount of computing time the number of collisions calculated is independent of the size of the system. For more realistic, continuous potentials this is also true. There one assumes that the forces are constant over some short time interval after which the forces are recalculated. The length of the time interval over which it is legitimate to assume constancy of the forces depends on the accuracy with which one wants to solve the equations. There are standard predictor-corrector methods with which these equations are solved which allow determination of the appropriate time interval.¹²

(a) Accuracy

One must make sure that the physical relaxation process one wishes to study has a shorter relaxation time than the time scale of build-up of numerical error. This is not always easy since it is amazing how rapidly numerical imprecisions accumulate. A simple demonstration of this can be obtained by running a system forward for a certain time and upon reversing all velocities

ascertain whether the system returns to its original state when it is run again for the same time. Even with twelve digit arithmetic for the simple hard sphere system, the time corresponds to only about 10,000 collisions, pretty independent of the size of the system. Different round-off errors lead eventually to a different collision history. One might argue that that should not affect the physical result since real systems are subject to random external effects as well; however, to be sure that the physical result is not affected, it is wise to run some calculations with higher accuracy, such as double precision, to make sure that the numerical noise does not dominate the longer physical rate processes that one studies.

The situation is particularly bad in stellar evolution calculations¹³ where most of the time the stars are weakly interacting through the gravitational potential and rarely strongly interacting through a collision. Furthermore, the system needs to be followed for a very long time. The accumulation of numerical errors is so severe (exponential growth) that most calculations have been dominated by numerical problems, putting the physical results in doubt.

(D) Thermodynamic Properties

In molecular dynamics, the energy as well as some other conserved quantities are continuously monitored to check on gross computer errors as well as round off errors. There is, hence, no problem in obtaining the internal energy. The pressure can be obtained through direct application of the virial theorem since the forces are known at each instant of time or through an indirect application of the virial theorem, namely through averaging by means of the pair radial distribution function. Although knowledge of the internal energy and the pressure over the entire density and temperature regime completely determines all the thermodynamic functions of the system, it would

be highly desirable to have a direct measurement of the other thermodynamic properties at a given state. Oddly enough, the numerical schemes can directly determine thermodynamic properties which are derivatives of the partition function, but not the thermodynamic properties which depend on the partition function itself, without some additional calculations. Thus, it is possible to get the Helmholtz free energy by integrating the pressure with respect to volume from infinite volume to the desired volume, but not by calculating it by means of the logarithm of the partition function, since the latter is unobtainable directly.

(a) Free Energy

A number of special techniques have been developed to circumvent this problem, particularly for the free energy or chemical potential since that quantity is very important in a number of applications. All these techniques depend fundamentally on the fact that the chemical potential is the derivative of the Helmholtz free energy w.r.t. the number of particles. Hence, the probability of adding an additional particle to the system is just the thermodynamic activity, whose logarithm is proportional to the chemical potential.¹⁴ The idea was used a long time ago in calculating the free energy of a system of charged particles by slowly turning on the charge of one particle. In general, integration over a "coupling constant" is called for, whose function it is to turn whatever potential one is studying on, all the way to full strength. In this way the free energy is identified with the reversible work necessary to add an additional particle to the system. Although this still calls for a series of computer runs for various strengths of the interaction, with a subsequent integration over this strength parameter, it sometimes is preferable over the volume integration

called for by the direct thermodynamic formulation.

The technique of determining the probability of acceptance of an additional particle is preferable whenever it is possible to do it. As pointed out earlier, that technique fails at higher density because the probability of acceptance becomes too low. This probability is determined by periodically stopping a molecular dynamics run for hard spheres, for example, and trying via many random tries to insert another sphere somewhere into the volume of the system. The probability of insertion is just the ratio of successful insertions, namely those that do not overlap with the other spheres in the system, to the total number of tries. In general, the activity is the average of the exponential of the energy change relative to kT caused by the insertion. Since at high density the overwhelming number of insertions lead to very unfavorable energy changes, it is not possible to obtain a proper measure of this probability and some other process, such as the coupling process, must be used.

Later, use will be made of another coupling process where each particle in the system is confined to a single cell which is then allowed to get larger and larger. In this way the free energy of a solid can be obtained by integration over the size of the cell. Such a molecular dynamics run would have hard sphere particles collide either with other particles as before or with the walls of the confining cell.

(E) Quantum Systems

So far only numerical procedures for the solution of the classical many-body problem have been discussed. The numerical procedures to solve quantum statistical mechanical problems are in a very much more rudimentary stage, and the problem is so complex that it taxes even the most advanced computers by presently available schemes. To permit the equilibrium quantum

many-body problems to be solved by a probabilistic method, the Schroedinger equation must be transformed into the form of a diffusion equation. This is easily done by transformation to an integral equation incorporating the relevant boundary conditions. That integral equation involves an unknown Green's function which must be first generated by a Monte Carlo game, after which the diffusion-like equation can be solved by another Monte Carlo game.¹⁵ This procedure has been successfully used to determine the properties of a few hundred Boson particles at zero degrees. Extensions to higher temperatures and Fermi statistics involve further enormous practical difficulties.

To study the more spectacular transport properties of quantum systems, the time dependent Schroedinger equation must be solved. This might be carried out via the so-called Madelung transformation which converts the Schroedinger equation to a Navier-Stokes type hydrodynamic equation, one for each particle in the system.¹⁶ One is then faced with the horrendously difficult task of the solution of a large number of coupled Navier-Stokes equations. In as much as these procedures are still in a very rudimentary stage with no physical insight of general interest so far forth-coming, the subject will not be pursued further here.

III. PHASE TRANSITIONS

One of the first problems to which these numerical techniques were applied was to the question of a solid-fluid phase transition for hard spheres. There had been some theoretical work suggesting such a transition, but of dubious reliability because of the approximations introduced. The significance of the proof of such a melting transition lies in whether purely

repulsive forces suffice, as had been suggested by more physically based models. Furthermore, if such a transition exists, the problem would have been reduced to its simplest and essential characteristic, giving hope that a rigorous theoretical proof would be forthcoming.

Theories of phase transitions represent one of the great challenges in statistical mechanics. As mentioned before, only the Ising model has so far yielded to that challenge. The difficulty is that the partition function has a mathematical singularity at the conditions of a phase transition beyond which the nature of the solution changes. There have been many suggestions of divergence of asymptotic series representations of the partition function at the conditions of the phase transition. One of these is the divergence of the virial expansion which represents the partition function in a power series in the density. The numerical results can shed some light on whether this density series might diverge and how reliable Padé approximants are in extrapolating such a series.

(A) Fluid Density

In as much as the first few virial coefficients were known, the hard sphere system was first run at sufficiently low density where the known virial series converged in order to check the numerical procedure. Once satisfied, higher virial coefficients were numerically obtained and the equation of state (pressure-volume-temperature relation) was extended to higher densities by the Monte Carlo and molecular dynamic techniques.¹⁷ One of the important facts that was learned in these calculations was that once more than 100 particles were used, the results no longer depended significantly on the number of particles; that is, the results did not change by more than about 1%, which is the typical numerical uncertainty in the results. Some studies were carried out to theoretically predict this

number dependence, but in general, that turns out to be a more difficult problem than to solve the actual infinite particle problem in the first place. Hence, the important conclusion which makes all these numerical simulation calculations so significant, namely that 100 particles represent the properties of an infinite system well in almost all situations, is based on such empirical observations.

The virial series represents the fluid equation of state well below a certain density. Beyond that density, using Padé approximants to extend the series proved to be a hazardous procedure. The problem is that there exist several Padé approximants by which to extrapolate and there is no theoretical guidance as to which one is best. These several Padé approximants all satisfy the general feature that they are the ratio of two polynomials which, when divided, reproduce the known virial coefficients. They differ in the degree of the polynomial in the numerator and denominator. However, all of them gave no indication of any discontinuity in the equation of state. Instead, they seem to follow continuously from the fluid phase into a glassy phase. This glassy phase is generated on the computer by slowly compressing the fluid phase, leading eventually to one of those isolated pockets in phase space spoken of earlier. For this "glassy" phase the pressure goes continuously to infinity as the system approaches a state of what might be called random close-packing.

Comparing the fluid properties with the prediction of the superposition approximation theory led to the conclusion that that approximation fails rather badly at high density and thus its veracity in the prediction of a phase transition must be questioned. On the other hand, the Percus-Yevick

or scaled particle theory, proved to be much more accurate and since the results can be expressed in simple analytical form, that approximation has become very popular, although the reason for its validity remain obscure and how to extend the theory has proved difficult. The hypernetted chain theory proved to be of intermediate accuracy compared to the above two theories. It is an interesting sidelight that, in general, the numerical work required to solve the above theories is of comparable magnitude to that for the numerically exact simulation procedures and this, usually, without assurance of a unique solution.

(B) Intermediate Density

At intermediate densities a peculiar behavior reminiscent of a phase transition was observed when the system was started initially in a solid or crystalline phase. After a very long computer run where the pressure fluctuated a small amount around the solid pressure value, the pressure suddenly jumped and fluctuated a small amount around the extension of the fluid branch of the equation of state. Only rarely did the pressure jump back down again. It was not possible to properly average over these two branches since transitions were too rare. The two branches were identified by various ways as fluid and solid by such measurements as the diffusion coefficients and, perhaps, most convincingly by a graphical display of the trajectories of the particles. These trajectories showed the localized excursion of the particles in the solid around their lattice positions and the accessibility of all of configuration space to the particles in the fluid phase.

This two branched behavior only occurred for systems of greater than about 30 particles.¹⁸ For fewer particles, the system stayed in

the solid branch even though it could be determined that particles were able to exchange lattice positions. The point seems to be that there were not enough particles present to create a disordered state, since after such an exchange in a few particle system the particles found themselves again in an ordered state. The lesson to be learned is that to obtain even the rudiments of a phase transition it is necessary to deal with a fairly large number of degrees of freedom. The only way that can be done analytically is by the introduction of collective coordinates, as will be illustrated shortly.

Going to much larger systems than 100 particles proved fruitless in three dimensions. Systems as large as 4000 particles have failed to show the coexistence of the two phases. However, in two dimensions, that is for hard disks, the effort was successful.¹⁹ Oscilloscope traces of the trajectories showed the coexistence of solid and fluid regions, and the equation of state in that region showed large pressure fluctuations whose average connected the solid and fluid branches by a van der Waals-like loop. Although for infinite systems it can be proven that such a loop cannot exist, for finite systems it is possible. The loop was analyzed in terms of the contribution of interfacial tension, which causes the predominant phase to force the particles in between the two different regions to take on more of its characteristics.²⁰ In this way, it is possible for a finite system to have a region which would be, for infinite systems, mechanically unstable, namely one where the pressure goes up as the volume goes up.

(C) Communal Entropy

The numerical hard sphere results allowed for the first time an evaluation of the so-called communal entropy that dispelled some of the

misconceptions previously held about it.²¹ The communal entropy concept arises from the difference between the properties of a system when it is treated in the one particle approximation and when it is treated as a many-body system; in other words, it is the quantity one was able only to speculate about previously. One thing that is known about it, however, is that in the high density (close-packed) limit of a hard sphere solid, the one particle concept is rigorously valid.²² On the other hand, in the low density limit the one particle concept leads to an error in the entropy, S/Nk , of unity; the error arises from the difference of a particle being confined to a region of a volume per particle as opposed to having the entire volume of the system accessible. This difference in the entropy, the communal entropy, must appear somewhere between the high and low density limit, and the logical place appeared to be at melting, when indeed the particles in the solid, confined to the neighborhood of a lattice site, are released upon melting from that restriction. The argument was considerably strengthened by the empirical observation that melting entropies for simple substances were of that magnitude. A detailed analysis revealed, however, that the communal entropy upon melting was only a small fraction of unity and that the communal entropy appeared gradually over the entire region from solid to gas.

The communal entropy concept could be utilized in two further ways. One of these was to predict the shift of the observed phase transition with the number of particles.²⁰ The nagging worry of the doubting Thomases about this hard sphere melting transition continues to be whether this phase transition disappears for infinite systems. It is hence necessary to understand how the transition depends upon the number of particles. Besides the decrease of the amplitude of the van der Waals-

like loop as the number of particles increases, as already discussed, the transition shifts in pressure and in volume difference between solid and fluid. The latter can be investigated, but will not be pursued here. The pressure shift can be understood on the basis of the communal entropy. This arises because the finite system of N particles in a periodic cell can be considered as differing in entropy from an infinite system by the communal entropy of N particles per cell.

The other use of the communal entropy was to establish the coexisting conditions for the solid and fluid phase in three dimensions, where sufficiently big systems could not be investigated on the computer to establish these conditions directly.²² What is hence necessary is to establish the free energy of the solid to be equated with the known free energy of the fluid. The way to accomplish that is by extending the solid branch of the hard sphere system artificially to low density by imposing the restriction of single occupancy. Single occupancy leads to a continuous extension of the solid branch to low density which upon volume integration of the pressure leads to a free energy all along the real solid region.

(D) Mechanism

There is little doubt that the phenomena observed on the computer corresponds indeed to melting. Using more realistic potentials than hard spheres, the phase transition observed on the computer could be well correlated with actual data. Furthermore, the phenomena could be understood on the basis of a well established empirical model of melting, namely Lindemann's law. That law, which gives a very good account of melting in all sorts of materials, states that a substance will melt

once its temperature and density are such that the root mean square displacement of a particle from its lattice site is about 10% of the lattice spacing. Both the hard sphere and disk systems correspond well to that rule. The problem now is to develop a model or a mechanism which accounts for this observation.

The safe and pragmatic view is that a substance melts once its free energy equals that of a liquid. Proposals for an instability in the solid associated with melting usually lead to an extension of the solid branch into the metastable region, or a van der Waals loop coexistence curve. The problem with instability theory hence is, that one has to find the first instability mode which, if not identical to the phase transition condition, lies at least closest to it. Furthermore, instability theories cannot identify the new phase formed. However, the universality of melting leads one to believe that there is a mechanism, namely one that destroys the long range order by an instability to a long wave length shear mode. Although there have been some arguments that this cannot hold for disks since there is no long range order, the arguments are deceptive. To be sure, it can be shown that no long range order exists in a two dimensional solid because the mean square displacement is infinite. This is because the system acts like a jelly. However, there is long range order relative to the position of any particle.

The search for a simple mechanism for melting led to a soft mode instability which can be mocked up crudely in a correlated cell model. In the two dimensional version of that model, alternate rows of atoms move collectively relative to each other. At the point where one row of atoms can slip past the neighboring ones, the model leads to a

discontinuity in the equation of state represented by a distorted van der Waals-like loop. The conditions at which the transition occurs in the model correspond nearly quantitatively to the ones found for disks.

A search for evidence that rows of atoms slip past each other in molecular dynamics calculations in the solid phase of disks very close to melting proved successful. The sliding rows consisted typically of 5 atoms each in two neighboring rows, where the end atoms jumped across the rows to close the loop. The loops got bigger closer to melting until finally one end no longer closed the loop. That created a defect in the solid which propagated very rapidly, leading to melting. There exists also some experimental evidence in the body-centered cubic phase of helium just prior to melting, that the heat capacity has a small contribution due to this collective mode. Usually that contribution to the heat capacity is unobservably small, but in helium a number of factors make it more favorable to observe it.

(E) Lattice Models

No theory has as yet been able to prove the existence of the melting transition for hard spheres. Such a proof remains one of the outstanding challenges in equilibrium statistical mechanics. The question one might then ask is whether it is possible to prove such a transition for lattice models, such as was used in the Ising model. For lattice models, such a proof might be easier because, as pointed out before, they involve a reduced space. In this case, the continuous configuration space would be replaced by a discrete space, or to state the problem mathematically, the integration over volume in the partition function is replaced by a sum. Replacing an integral by a discrete sum is done all the time in numerical integration and as the

mesh or grid is made sufficiently fine, the approximation to the integral can be made as accurate as desired. The analytical problem, however, is that for fine meshes the integral can no longer be managed. The only lattice problems that have been solved correspond to mesh points comparable to the number of particles in the system. In other words, unless a grid spacing comparable to the size of the particle suffices, the evaluation cannot be handled analytically. The unfortunate fact is that such coarse spacing seriously distorts the partition function in dense fluids and hence the phase transition can not be adequately described by practically workable lattice models.

A one-dimensional model using hard rods can demonstrate the limitations very simply, since its partition function can be worked out exactly, no matter how fine the grid.²⁵ At typical melting conditions, the spacing between particles, as Lindemann predicts, is about 10% of the size of a particle. Under these conditions, in order to evaluate the partition function accurate to 1%, that 10% space must be covered by 50 grid points or there must be 450 grid points to cover the space occupied by each particle. In three dimensions that number must be cubed, and with that mesh size only 1% accuracy is achieved, and even then it is not assured that the narrow passages in phase space between the fluid and solid pockets might not be missed. At the critical point, where the lattice theories have been much applied, the situation is not nearly as bad. At the critical point the spacing between particles is comparable to the size of the particle itself. In order to get 1% accurate thermodynamic properties, it would be necessary to cover a particle with only 50 points in each dimension, still way beyond analytical capabilities.

However, by covering each particle and each of the spaces in between particles by at least one grid point, as is typically done, one might hope to get at least the qualitative behavior correct, particularly for the very important long range behavior of the spacial correlation functions. These correlations, being of a range much larger than the size of a particle, should not be qualitatively dependent on the grid size as long as it is also of the size of a particle.

The lattice models, nevertheless, have found two useful applications in dense systems. One is that they can provide both upper and lower bounds for the partition function. The bounds for hard rods derive from the simple observation that if one measures the non-integral length of a line by a discrete number of equal sized elementary lengths that fit in it, one always overestimates the length. The average error due to edge effects is just one half of the length of one of these elementary length, and it is this fact which led to the error estimates. The other practical application is that no matter how fine the grid, the lattice model gives the wrong behavior in the close-packed limit, where the space between the particles shrinks to zero. Thus, the computer calculations with their exceedingly fine grids, determined by the number of significant digits with which the positions are specified, cannot properly determine the properties of dense systems very near close-packing. This has not been a serious limitation, and, in fact, through the computers it has been possible to establish the correct asymptotic behavior of hard sphere solids.²² This will be discussed in connection with critical behavior in solid systems.

IV. VAN DER WAALS MODEL

One of the results of the numerical work has been to gain more insight into the validity of the mean field models of which the van der Waals model is a prime example. The van der Waals model, which is now just over a hundred years old, was neglected by theorists for a long time during which they grappled with many unphysical models as they tried to cut through, mostly unsuccessfully, the mathematical difficulties by approximations that would make the mathematics tractable. These efforts ignored the mounting empirical evidence that the van der Waals model correlated the experimental data remarkably well outside the critical region. The numerical work circumvented these mathematical difficulties, showed the validity of the van der Waals model in the asymptotic high temperature limit for particles with a hard core interaction potential, showed that the corrections to the model were small, and showed that all three phases of matter could be obtained by that model.

(A) Perturbation Theory

As a matter of fact, the usefulness of the van der Waals model and its corrections from a numerical point of view transcends its usefulness as a physical model. From a numerical point of view, it is highly desirable to overcome the limitations of numerical calculations that they are specific to all the conditions imposed in the solution. One of these conditions is the choice of the specific interaction potential between a pair of particles, for example, the hard sphere potential. It would be very valuable if this specific solution could be extended by analytical means to a class of slightly different interaction potentials, for example, those which have a weak attractive potential added on to the core. It turns out that if this

attractive potential is sufficiently weak so that first order perturbation theory suffices, and sufficiently long range so that this perturbation theory can be extended over the entire density regime, one recovers rigorously the van der Waals model.²⁶ Such a perturbation theory will not only lead to the gas-liquid coexistence region for which it was originally proposed, but also to the solid-fluid phase transition region, since, as has just been seen, this is contained in the hard sphere system by itself. Without the addition of attractive forces, the hard sphere fluid cannot distinguish between a liquid and a gas phase.

Having a rigorous proof on the conditions under which the van der Waals model is valid, it is now of interest to ascertain what the corrections to the model are when these conditions are not met, since for many realistic potentials the conditions on the range and strength of the attractive potential are far from being met. The limitations imposed by the short range of many realistic attractive potentials can be overcome by restricting the density range over which the van der Waals model is applicable. At sufficiently high density (for practical purposes usually greater than the critical density of a substance) the mean space between particles is sufficiently small compared to the range of the attractive forces, so that the particles rarely escape the interaction potential of their neighbors, which, in effect, provides the mean potential. One must investigate why, in spite of the large value of parameter of the perturbation expansion (the strength of the attractive potential relative to kT) the model gives accurate results when only the first term, that is the van der Waals model,

is used. For typical liquid conditions the parameter of the potential relative to kT is of the order of unity and hence the precision with which the van der Waals model describes the liquid state means that the higher order corrections must be small.

(B) Pure System

There is a well founded statistical mechanical theory for each coefficient of the power series expansion in the perturbation parameter.²⁷ The latter is the reciprocal of the reduced temperature; that is the temperature reduced by the strength of the attractive potential. For evaluation of each successive coefficient in this expansion, higher order correlation functions of the unperturbed system must be known, or equivalently, higher order fluctuations in the attractive potential about the mean (more precisely cumulants) must be evaluated.²⁸ The latter approach is numerically much more convenient since it avoids having to tabulate highly dimensional correlation functions for the unperturbed system. As is typical of perturbation theory, each successive term requires more detailed information about the unperturbed system, which, in this case, must be numerically obtained.

As expected, even the first correction to the van der Waals model made only a small contribution. This is the square term in the reciprocal temperature, involving quadratic fluctuations about the mean potential. The reason that the still higher order terms are negligibly small was found to be due to the near Gaussian character of the fluctuations. For a Gaussian distribution the higher order cumulants can be shown to be strictly zero. The half width of the Gaussian distribution, needed for evaluation of the first correction to the van der Waals model, was found to be remarkably insensitive to density over the entire fluid range; corresponding to a root

mean square fluctuation of about half a particle around the mean of about twelve particles at normal liquid densities. At lower densities the mean number of particles within the range of the attractive potential decreases to about three particles near the critical density of a fluid; however the fluctuation about this lower mean is still about half a particle. The reason for the relative larger fluctuations at the lower density is, of course, the looser packing of the hard spheres. It is, hence, entirely a matter of the geometric behavior of hard spheres that leads to the near volume independence of the Gaussian half width for typical ranges of the attractive forces. The significance of the volume independence is that it makes that quadratic correction term to the van der Waals model negligible for the equation of state. Since the still higher order terms were negligible in the first place, the validity of the mean field approximation, even for strong attractive forces, can be understood.

Only near the critical point, where the fluctuations are large, does this expansion not converge. The hard sphere system has no premonition of such large fluctuations and hence it is not surprising that it does not even give the qualitatively correct singular behavior of the critical point. Neither does a finite system of particles interacting via a realistic potential, when studied by the Monte Carlo or molecular dynamics method. The critical singularities are distorted by any calculation that constrains the long range fluctuations. Nevertheless, these calculations or the perturbation calculation can locate the critical point occurrence as to pressure, volume and temperature very well.

(C) Mixtures

There were several interesting questions regarding mixtures that could be pursued by numerical calculations. One of these concerns the possibility

of the existence of two fluid phases for mixtures of hard spheres. This could be ruled out on the basis of these calculations.²⁹ In fact, it was found that these mixtures of spheres behaved nearly ideally. Their non-ideality could be identified with a small negative excess volume of mixing, that is the volume of the mixtures was slightly smaller than the sum of the two volumes of the pure hard spheres systems that are mixed. This corresponds to the elementary observation that it is possible to pack mixtures of spheres slightly more efficiently than the pure spheres separately. The near ideality of these sphere mixtures does not correspond at all to what is found in real mixtures, so that we conclude that the attractive forces play an essential role in determining the excess properties of mixtures.

Hence one is led to an application of the van der Waals model to mixtures. Though that model does very well in the prediction of the qualitative features of mixture properties, as shall be discussed in the next section for gas-gas phase separation, it leaves something to be desired in its quantitative aspects. The reason for the greater inadequacies of the van der Waals model for mixtures than for pure systems is readily apparent. In the first place, the excess properties, representing a difference, are generally an order of magnitude smaller than the pure properties, thus higher precision is required to predict them well. Secondly, deviations from the mean field theory are not only due to potential fluctuations as in pure fluids, but also due to concentration fluctuations. These have been ignored or were poorly represented in previous mixture theories that tried to improve upon the van der Waals model. Testimony to that fact is that no previous theory gave significantly better results than the van der Waals model. That model necessarily assumes random mixing; whereas in real mixtures, particularly

when phase separation is approached, significant clustering must occur.

This clustering, corresponding to concentration fluctuations, can be accounted for by calculating the corrections to the mean field model in the perturbation series.

Although that series can account for the major quantitative defect in the van der Waals mixture theory, the convergence of the series is not as fast as one would like. This shows up particularly in the heat capacity, which is entirely dependent on the fluctuations; the van der Waals model predicting zero excess heat capacity. In fact, due to large concentration fluctuations, the heat capacity in a mixture is frequently larger than the sum of the separate heat capacities of the pure components at the same density and temperature as the mixture.³⁰ The first correction to the van der Waals model, the quadratic term in the fluctuations, cannot account for this phenomena, so one is forced to go to higher order in the series. Instead of performing these rather time consuming numerical calculations, an effort was made to reorder the perturbation series in powers of the reciprocal temperature by graph theoretical techniques so as to achieve faster convergence.³¹ In this way, certain classes of graphs occurring in each term of the infinite reciprocal temperature series was summed, such as ring graphs, for example. The evaluation of these graphs does not require more knowledge about the unperturbed system than is already necessary for evaluation of the mean field. The disadvantage of this method is that one loses the simple power series behavior in temperature and that one no longer has a simple parameter characterizing the expansion. The latter difficulty is related to the well known problem of ordering sets of graphs according to the magnitude of their contribution. One can, however, use physical arguments to show why the summed graphs

make the dominant contributions and the omitted ones are of lower order. The test of such an approach lies in its predictive power and judging by the calculation of the heat capacity of mixtures, the approach proved very successful. Thus, the numerical approach was able to pinpoint the type of correction required to the van der Waals model of mixtures, and a relatively simple graph theoretical calculation was able to account for it, making deviations from random mixing calculable.

V. SYSTEMS WITH CRITICAL BEHAVIOR

As was mentioned before, the numerical schemes dealing with a finite number of particles seriously distort the nature of the singularity at the critical point which crucially depends on the large distance behavior of correlations. Thus, it cannot be expected that the exponents signifying the nature of the singularity at the critical point can be realistically obtained. One might, however, again ask how large the system has to be in order to approximate the macroscopic system well with respect to the onset of the singularity close to the critical point. In other words, is it possible to observe deviations from classical (van der Waals) behavior close to the critical point for the very small systems that can be investigated on computers. Sufficiently far from the critical point, the fluctuations might be small enough so that these finite systems might realistically represent them and yet the fluctuations are not so small that the mean field theory predictions are accurate.

Very little work has been done in this connection because of the enormous computer time requirements to get sufficiently precise results. A very preliminary investigation shows promise that such an investigation

might be fruitful for some properties.³⁸ The results indicated that the pressure-volume-temperature relations on the coexistence curve around the critical point had too small a deviation from classical behavior to be observed within the accuracy of the data. However, the heat capacity did show enhanced values in the critical region that are inconsistent with mean field theory predictions. Extracting an exponent from this numerical data in a fashion analogous to the way real data is handled, led to a divergence consistent with what is experimentally observed. The conclusion appears to be that small scale fluctuations significantly contribute to the heat capacity some distance away from the critical point and they can be quantitatively evaluated in small systems. Closer to the critical point, the heat capacity for these finite systems does not assume the large values found experimentally, again because the large scale fluctuations that are ignored have a large effect.

(A) Solid-Fluid

The computer methods have been applied in a number of cases to the question of whether a critical point exists, ignoring the nature of the singularity. One of these examples concerns the question of the existence of a solid-fluid critical point. The previous work on the hard sphere solid-fluid phase transition showed that if the intermolecular repulsive potential is sufficiently repulsive, there is no such critical point since it was found that at sufficiently high density, no matter what the temperature, a solid phase is formed. Since real systems have softer repulsive potentials than hard spheres, the question is then whether for these a solid can always be formed. The hard sphere calculations were, hence, repeated

for the repulsive Coulombic potential, which represents the interaction potential between atoms at very high pressure, once the electronic shell structure has been pressure ionized.³² The electrons can then be considered as forming a uniform background in which the charged nuclei swim. These nuclei, because of their heavy mass, behave classically and interact via the softest known repulsive potential, namely the Coulombic one.

This potential, because of its long range nature, must be handled with some care in finite systems with periodic boundary conditions. It can be shown that better results are obtained at high density, if one abandons periodic boundary conditions and instead considers the finite system as constituting a unit cell, periodically repeated, to form an infinitely large crystal. The practical difference is that a particle not only interacts with all the particles in the cell but also all their periodic images. The contribution of the periodic images is evaluated analogously to the methods used in evaluating potential contributions in ionic crystals, namely by the Ewald lattice sum method. The use of the more complicated boundary conditions slows the calculation down, but not prohibitively.

The results were that again a solid is formed when the potential energy of the system exceeds a certain multiple of the kinetic energy. That multiple is not of the order of unity as it is with most ordinary materials, but about a factor of one hundred larger. Nevertheless, the melting transition is still well described by the Lindemann law in the sense that melting occurs when the root mean square excursion distance from a lattice site is about twenty per cent of the lattice spacing. This is to be compared to the ten per cent value for more repulsive potentials.

(B) Coulomb Gas

Although these results lead to the conclusion that no solid-fluid critical point exists, one must, at sufficiently high density, consider that the nuclei start to behave quantum mechanically. At these very high densities, it can easily be shown that the zero point energy must eventually exceed the lattice potential energy of a Coulombically interacting system. This is because the zero point energy rises as the reciprocal square of the lattice spacing while the potential energy rises only as the reciprocal lattice spacing itself. Thus, there is a density even at 0°K above which a solid cannot exist. This density corresponds to a lattice spacing of about 0.1 Bohr radius for protons and is obtained by an approximate numerical calculation, since the full quantum mechanical many-body solution procedure is as yet too cumbersome to be practical.³³

The scheme involves approximating the total wave function as a pair product wave function of a specified functional form. The form involves a few parameters, which have to be optimized variationally. This can be achieved by a series of classical Monte Carlo calculations with the introduction of a fictitious interaction potential related to the specified pair wave functions. This approximation has been shown to be quite adequate in explaining the melting transition in helium.³⁴

The conditions under which the Coulomb gas has been found to melt, again corresponds quite well to Lindemann's law, except that in this case, the particles oscillate about their lattice position due to zero point energy instead of thermal energy. A melting curve for the quantum Coulomb gas can be obtained at other than 0°K by utilizing Lindemann's law, where the excursion distance is a result of a combination of zero point and thermal

motion. This leads to a closed region in density and temperature below which a solid exists. The surprising prediction of this theory is that for protons above about 3000°K it is not possible to have a solid. That temperature is very low by astrophysical standards and indicates that most protonic stars have liquid interiors. This does not appear to be true for pulsar for which star quakes seem to be observed. Hence, either the potential or the density do not conform to the above conditions in these stars.

It should be emphasized that the limited region over which a solid is stable in a Coulomb gas does not imply the existence of a critical point as it is usually understood, namely an existence of a phase transition which is less than first order. It can be argued that such a transition would implausibly imply that one could continuously go from a solid of long range order to a fluid of short range order. The above calculations, in fact, predict a first order solid-fluid transition.

(C) Helium

Another prediction, very similar to the above, of a closed solid region of stability is in the case of helium. In this case, the solid region is surrounded by another solid phase and again the transition is characterized as first order and a temperature above which the specified crystal structure cannot exist.³⁵ The reason for taking this system up briefly here is to point out that such a phase transition is extremely hard to study numerically because the difference between the two crystal structures is so extremely small. The two crystal structures, face-centered-cubic and hexagonal -close-packed are so similar that numerical methods have not yet established their relative stability. A determined effort was made to establish for classically behaving hard

spheres which of the two phases would be stable as a function of density.³⁶ The free energy difference could not be reliably established. Even at high density where special methods related to the single occupancy calculation were used to calculate the coefficients of the expansion in the free volume, the first two coefficients proved to be the same within 5 significant numbers. The third coefficient, but not outside statistical error, favors face-centered cubic. For a harmonic oscillator it can be shown by still other numerical methods peculiar to that potential, namely by the solution of the Born-van Karman matrix for the frequency modes, that the face-centered crystal is stable.³⁷

The above calculations of the stability of the face-centered cubic phase in the high temperature classical region agrees with experimental observations on helium. The stability of the hexagonal crystal structure of helium at low temperature is no doubt due to the quantum mechanical nature of these crystals. In fact, it can be rigorously proven in the single occupancy approximation for hard spheres, by making use merely of the symmetry of the crystal, that at low temperature the hexagonal phase is more stable than the face-centered phase.³⁸ Thus, hard spheres are likely to exist in at least two different crystal structures, but to establish the phase transitions by numerical techniques requires higher precision methods than are presently available for even the simpler classical calculations. In this connection it is worthwhile to point out that hard spheres are not stable in the body-centered phase, at least classically. This phase is also known to exist for helium, but its stability in a classical system requires at least non-nearest neighbor forces.

In confirmation, a body-centered crystal of hard spheres partially melts at any solid density when investigated by numerical means.

Another interesting point emerged from the study of hard spheres at high density. This is a value of the entropy at close-packing, which is a measure of the free volume available to a sphere.³⁹ It turns out that the self-consistent model makes an enormous error in that estimate. A much more accurate value is obtained by the so-called Lennard-Jones Devonshire model which allows a central sphere to have access to the entire volume of a cell formed by holding the nearest neighbors fixed at their lattice positions. The moral appears to be that self-consistency is not always advantageous from a quantitative point of view. Disappointing too was the slow convergence of various solid cluster theories that tried to estimate this free volume more accurately by calculating corrections to the single particle cell models.

(D) Electronic

The numerical calculations can also help to elucidate certain electronic transitions which are known to have real critical points in the solid phase. Such a critical point is believed to be possible only in the solid phase if the transformation is between two identical crystal structures. The only known example, namely cerium, conforms to that. The transformation is believed to be caused by the stability of a different electronic configuration of the atom in the two phases. The change of electronic configuration with pressure comes about because of the shift of electronic energy levels when the atom is confined to a smaller space. Confinements favor those energy levels where the wave function has a

higher probability to be, so to speak, inside the atom. For present purposes, such a sudden shift in electron configuration can be idealized as a sudden shift in the radius of an atom. Thus, a numerical study with a two step hard sphere interaction potential, that is a repulsive square well potential, might mock up this physical situation well.

Although little work has been carried out for such a potential as yet, it can be predicted that if the change of radius is less than 10%, the system might show a critical point. This is because, recalling Lindemann's law, a solid system can 'average' over such distances before it melts. If the radius change is larger than 10%, then one would predict that the solid-solid phase transition extends all the way to melting. Upon melting, however, the phase change would disappear since a liquid can 'average' over such distances. One would, in fact, predict a melting maximum in the neighborhood of the solid and melting phase line intersection. There is one known example of this, namely cesium, which is likely to have a very large size change in its electronic transition. In any case, the numerical calculations with such potentials could confirm the prediction that no first order phase change would be observed in liquids. There is no known observation of one.⁴⁰

(E) Gas-Gas

For mixtures, the critical point of pure systems becomes a critical line in the pressure-temperature plane. Gas-gas critical behavior is then said to occur if this critical line reaches temperatures greater than the critical temperature of either pure component. The conditions under which such behavior can occur has been worked out long ago through the

van der Waals equation. Experimental confirmation of this phenomenon is also quite old. The criterion for which this effect will be observed requires that the mixture consists of two components with largely different attractive forces. With the revival of interest in the critical point of mixtures, particularly tricritical points, it is worthwhile to point out that the numerical procedures can also be utilized to make more accurate predictions of critical lines and their intersection than the van der Waals predictions!⁴¹

VI. TRANSPORT PROPERTIES

(A) Previous Models

The first numerical effort in the study of transport properties went into critical tests of existing models. One of these models proposed that transport in fluids was primarily of the type occurring in solids with vacancies. In such a solid a particle would typically oscillate for long periods of time around its lattice position and occasionally, when it is near a vacancy, make a jump of the order of a lattice spacing into the vacancy position. A critical test of this mechanism appears to be a study of the distribution of free paths in a fluid. The free path in a hard sphere fluid is the distance a sphere traverses between successive collisions. If the above model were applicable, one would expect this free path distribution to be bimodal. This is because one would expect two characteristic distances to be of importance, namely the small distance corresponding to the free length and the one corresponding to the average spacing between centers of particles. Instead, the free path

distribution showed no significant structure.⁴² It proved to be nearly exponential with distance and nearly independent of density when scaled by the mean free path. Thus, from this evidence, there appears to be no significant new mechanism of transport in dense fluids. The simple kinetic theory valid at low density describes the free path distribution well at all densities.

Another model proposed that the trajectory of a typical particle consisted of two unrelated parts, namely hard sphere collisions that could be described by kinetic theory and interaction with the attractive potential in between the hard core collisions that could be described by Brownian motion. The use of Brownian motion was thought to be applicable because the interaction with the attractive potential was thought to be weak and frequent. A numerical study of the frequency of interaction with the attractive interaction in a square-well system revealed that such interactions were rare at fluid densities.⁴² In a typical liquid, the majority of successive hard sphere collisions were found to be uninterrupted by an attractive interaction. In fact, this study led to the conclusion that the essential characteristic of transport in liquids could be understood if transport coefficients for hard spheres could be calculated. This is in conformity with the accuracy of the mean field approximation for equilibrium properties. In the mean field approximation, the attractive potential does not affect the transport properties at all, since a constant potential cannot exert a force and, hence, affect the trajectory of a particle. These preliminary numerical studies, hence, proved the linear or free flight trajectory model to be the most appropriate.

Hence, a detailed study of hard sphere transport properties was undertaken.

(B) Comparison to Experiments

Just to make sure of the validity of the hard sphere model, a comparison with experiments was undertaken using an approximate hard sphere transport theory.⁴³ That theory, developed by Enskog, assumes that the transport coefficients calculated at low density, where the Boltzmann equation is assumed to be a valid description, can be scaled to higher density by merely scaling the time between collisions. Just as the free path distribution was found to be accurately scalable by the mean free path, so it is assumed that if there is no new mechanism of transport with density, the transport coefficients need only be scaled in time owing to the fact that the collision rate increases with density. Since the collision rate can be directly related via the virial theorem to the equation of state previously determined, the comparison to experiment on such substances as the rare gases could be easily carried out. The result for the diffusion coefficient, the viscosity and the thermal conductivity was in agreement within about 10% in the dense fluid region. Applicability of the model, just as in equilibrium, is restricted to the dense fluid region and, in fact, the single parameter necessary for this experimental comparison, namely, the hard sphere diameter, was obtained from thermodynamic data analyzed by means of the van der Waals model. By using the somewhat empirical scheme of making the hard sphere diameter temperature dependent to account for the softness of real repulsive potentials, the temperature dependence of the transport coefficients could also be well explained without invoking the customary device of an activation energy. It is

this latter concept which had been disproved by the free path study.

(C) Perturbation Theory

The conclusion from this study is that the correlations in the hard sphere systems, omitted in the Enskog theory, make a small contribution to the transport coefficients. The small deviations that were observed in the experimental comparison are certainly also partially caused by the neglect of the attractive forces in the hard sphere model. Thus, it is not only necessary to get accurate properties for hard spheres by molecular dynamic computer studies, but to develop a perturbation theory for the attractive potential, just as for equilibrium properties. The latter theory has met severe obstacles.

The basic difficulty is that a small potential perturbation can in certain circumstances lead to vast changes in the trajectory of a particle. For example, such a small perturbation can, by bending the path of one particle a small amount, cause two hard spheres to collide which would not have otherwise, changing the whole subsequent history of the system. Another example is that a small potential perturbation can lead to orbiting in what would have been without such a perturbation a glancing encounter. Although some individual trajectories can thus be vastly changed, it is known from the above experimental comparison, that on the average, the attractive potential has a relatively minor effect. The difficulty appears in the theory through divergences in the perturbation expansion when it is applied directly to the individual trajectories. It is, hence, necessary to perform the averaging over the trajectories first, before carrying out the attractive potential perturbation. When that is done, the expansion

series is no longer a simple power series in reciprocal temperature.³⁰

From a numerical point of view, it has not been possible to get an explicit expression for the coefficients in the perturbation expansion, or in fact, the form of the expansion. Instead, one is forced to the cumbersome device of calculating the transport coefficients by molecular dynamics at several high temperature values, for example, for a square-well potential, and from that data by differencing schemes extract the expansion coefficients.

(D) Method

There are two basic approaches by which to determine transport coefficients by the numerical schemes. One is analogous to the typical classical experiment whereby an external gradient is imposed.³ Since this necessarily involves imposing steep gradients on such small systems so that a flow can be determined outside statistical fluctuations, these calculations are not favored. Other disadvantages are that frequently artificial boundary conditions must be imposed and that only the transport coefficients themselves, and not the detailed correlations underlying them, can be obtained. This, coupled with the fact that these calculations are not even computationally significantly faster, has led to the use of the fluctuation-dissipation approach. This approach is also increasingly being used to determine the transport coefficients experimentally.

Taking the simplest transport coefficient as an example, the diffusion coefficient is defined as the long time limit of the mean square displacement of a particle in an infinitely large system divided by the time. It has always been cautioned by the careful investigator that this limit will only exist, that is that the diffusion coefficient is a constant, if the particle forgets its past history sufficiently fast. The usual argument presupposes

that after a sufficiently long time has elapsed, the particle assumes a stationary Markov process, that is it executes the random walk of a drunkard, for which this limit can be proven to exist. There are, of course, well known examples where this does not occur. One is the perfect gas in which a particle never collides, so that the distance it travels is proportional to the time elapsed. Hence, the diffusion coefficient diverges linearly in time. At the other extreme is the particle bound by a harmonic oscillator. In that case, the particle is confined to a finite region in space, and the diffusion coefficient vanishes in the long time limit.

The above expression for the diffusion coefficient is called the Einstein expression and there exist equivalent ones for all the other transport coefficients and these have, in fact, been programmed on the computers.⁷⁴ A single trajectory in equilibrium phase space is run, and the mean of the square of the displacement for the diffusion coefficient, for example, is determined by chopping this single trajectory up into a number of equal segments. Each initial state of these segments can be considered as another member of an ensemble. Alternatively, averaging can be achieved by generating members of an ensemble by the Monte Carlo method whose time evolution is subsequently followed by molecular dynamics.

(E) Autocorrelation Function

Although a rigorous proof of the identification of the measured transport coefficients with the theoretical Einstein expression is lacking, there is no difficulty showing the equivalence of the Einstein expression to an autocorrelation function expression. By straight forward mathematical

manipulations one can show the equivalence of the mean square displacements over time to the time integral of the velocity autocorrelation function, provided the diffusion coefficient itself exists. This equivalence has also been shown numerically and sometimes one or the other expression is preferred for technical reasons. For discussion purposes, it is preferable to speak of these autocorrelation functions, because they show most clearly the effect of correlation. More precisely, the deviations of these autocorrelation functions from the exponential behavior predicted by the Enskog model of uncorrelated events, reveal what the dominant correlations are that have to be accounted for in a more accurate theory of the transport coefficients of hard spheres.

Very little is rigorously known about these autocorrelation functions. The Enskog theory predicts rigorously only the initial slopesince for very short times no correlations can build up. The next term in the Taylor expansion in time of the autocorrelation function already involves ternary collisions which could be correlated through such cyclic events as particle 1 colliding with 2, 2 with 3 and subsequently 3 with 1 again. This contribution, which Enskog neglects, is already hard to calculate. The numerical work confirmed the very early time behavior as predicted by the Enskog theory, and showed that the relaxation time determined by it, when introduced into an exponential autocorrelation function, reproduced the full autocorrelation function fairly well.

Although the deviations from exponential behavior found by molecular dynamics were small, they were of a puzzling nature at intermediate densities.⁴⁵ At high densities, the velocity autocorrelation function became negative, as expected, due to the solid-like character of the fluid, which causes

the velocity of a particle, on the average, to be reversed after a few collisions. At intermediate densities, however, the velocity correlations were positive and lasted for many collisions. A typical particle seemed to persist in its original direction of motion after having undergone many collisions. To be sure, the persistence was quite weak, at a level of about one one hundredth of its original velocity, but such that it led to a significant dependence of the result on the number of particles used in the molecular dynamic computations. This number dependence, which for more than one hundred particles is usually hardly detectable, as well as the long nature of the persistence indicated that a highly collective effect was involved.

(F) Hydrodynamic Model

After some false starts, this persistence was eventually quantitatively explained as being due to a hydrodynamic vortex mode.⁴⁶ The hydrodynamic model that was used involved a moving volume element, representing the particle, in an otherwise stationary viscous, compressible medium, representing all the other particles of the system. The moving volume element pushes the fluid ahead of it and leaves a smaller than average pressure behind it. The pressure equalized by the generation of a compressional sound wave ahead of the volume element and a dilational one behind it. The speed with which this sound wave propagates depends on the compressibility, but in any case does not lead to any persistence. The pressure can, however, also equalize by the generation of a double vortex flow around the moving volume element. At long times, this flow dominates since the sound speed by simple dimensional arguments can be shown to propagate faster than the diffusion of vorticity.

The vortex flow leads to positive persistence, since some of the momentum transferred to the medium is fed back into the particle itself. On a molecular scale, the particle collides with the neighbor ahead of it, which subsequently collides with the other neighbors such that some of the original velocity is returned. One then expects that the maximum positive persistence should appear when approximately 10 collisions, corresponding to the number of nearest neighbors at liquid densities, have occurred. The numerical results verify this expectation and furthermore show that at lower densities the maximum persistence appears at fewer collisions, till at very low densities, the persistence is so weak that it cannot be observed. The clinching numerical verification of these ideas was a determination of the velocity field itself.⁴⁷ This was determined by a study of the velocity correlations between a particle and its neighbors at various positions relative to that particle at various times. Clear evidence of a double vortex field at a later time was obtained.

(G) Divergence

The hydrodynamic model required the solution of the Navier-Stokes equation for the given initial conditions. An analytical solution is only possible at large times. Dimensional arguments at large times showed that the velocity autocorrelation function decays as the reciprocal time to the dimensionality of the system divided by two. Hence, the correlations do not decay exponentially as previously expected and, in fact, in two dimensions decay slowly enough so that the diffusion coefficient diverges. A computer study of the detailed behavior of the autocorrelation function in two dimensions at long times confirmed not only the power law decay of reciprocal time but also the proportionality constant of that decay.⁴⁶ In three dimensions

the systems were not quite large enough to observe the asymptotic decay, because boundary interference effects spoiled that observation. The sound as well as the vortex waves constructively interfere at periodic boundaries; an effect which could be quantitatively accounted for. With still larger systems, however, these effects can be sufficiently delayed so as to observe the power law decay in three dimensions as well.

For shorter times, the Navier-Stokes equation must be solved numerically and the numerical solution can be compared both to the vortex field and the velocity autocorrelation. The comparison worked well except at very short times; less than the time corresponding to a few collisions. For such short times, the hydrodynamic model is just not applicable. It is necessary to consider the detailed molecular structure of the fluid. To be sure, by the use of generalized hydrodynamics, which uses time and space dependent transport coefficients in the Navier-Stokes equation, it is possible to apply hydrodynamics at a shorter time scale, but still not at a level of a time between collisions. In fact, the remarkable aspect of these calculations is that the usual hydrodynamics is already valid at such a short time and distance scale, namely at the time corresponding to the order of 10 collisions per particle and a distance scale of the order of a few molecular diameters. Previously it was thought that the molecular and hydrodynamic time scales were far separated. The fact that they are intimately mixed is the real novelty of the molecular dynamics results. The other is the applicability of the hydrodynamic model to the description of the correlation. The model itself has been studied long ago by Stokes.

The three dimensional behavior of the autocorrelation function leads to a convergent diffusion coefficient, however, previous theories have to be

modified since they all assumed the validity of a Markovian description at long times. The previous theories can be recovered by projecting out the hydrodynamic part, although, as pointed out above, the separation is not clean cut. Another way to obtain the long time behavior is by means of graph theoretical techniques. These techniques had previously given indication of unusual behavior in the calculation of the density corrections to the Boltzmann low density results. These corrections were shown not to be expressible in a power series in density but involved logarithmic terms in the density. These arose because whole classes of ring diagrams had to be summed in order to get convergent results. For the long time behavior, ring diagrams to all orders must also be summed. These are similar to the cyclical correlations mentioned earlier and the physical analogy to vortex motion is tempting, although this connection has not so far been clearly established.

In two dimensions, because of the divergence, the situation is much more confusing. Neither the Boltzmann equation nor Navier-Stokes hydrodynamics is valid and a new formulation has not yet been clearly found. Even the long time behavior of the velocity autocorrelation function is not known for certain. Although the molecular dynamics calculation established the reciprocal time behavior, which has been confirmed by both the hydrodynamic model and graph theoretical resummation techniques, it is unlikely the correct behavior, in as much as the computer calculations are restricted to small hydrodynamic times and the graph theoretical techniques have similar restrictions. The theoretical hydrodynamic result cannot be believed because it assumes the validity of the Navier-Stokes description which is

the very thing that has been proven inapplicable. The realization of this dilemma manifests itself in the assumption of the existence of a viscosity. The viscosity and thermal conductivity (at least their kinetic parts) can be shown to diverge also in two dimensions. These transport coefficients have a kinetic as well as a potential part, and whether the potential part diverges is at the moment still an open question.⁴⁴ In any case, the divergence of the kinetic part of the viscosity puts the asymptotic behavior of the velocity correlation in doubt. A hand waving, self-consistency criterion predicts a velocity autocorrelation divergence as the reciprocal of the product of the time and the square root of the logarithm of the time.⁴⁸ Such a behavior would also be consistent with the limiting long time behavior observed by molecular dynamics, since it is numerically impossible to distinguish this behavior from that of reciprocal time.

(H) Brownian Motion

There are some interesting considerations as to what happens to this vortex correlation as the mass and size of the diffusing particle varies. Both in the limit of very light and very massive particles this correlation should disappear. In the Lorentz limit, that is the light particle, the particle scatters among a set of stationary particles and, hence, does not have the momentum necessary to generate a vortex. An interesting question is then whether such a light particle still has a slowly decaying velocity correlation function. Such a slow decay has been found for a perfect gas particle scattered from particles of square-shape in two dimensions.⁴⁹

The origin of this decay is not related at all to the hydrodynamic vortex mode, but arises from trajectories which after many scattering events return the particle to its origin. The long return paths are intimately connected with the geometry and dimensionality of the scatters and it would be interesting to study

these correlations for scattering from spheres. Such studies could determine the size above which the light particle is trapped among its neighbors at any given density. At that size, the diffusion coefficient would vanish because of the high probability of backscattering. The velocity autocorrelation at that point does not necessarily have a long tail. Furthermore, the Enskog theory fails badly because of the neglect of backscattering in that theory.⁵⁰ A more appropriate theoretical model would be a percolation model.

For the massive particle, that is the Brownian motion limit, the persistence should be enhanced. However, in the infinite mass or stationary particle limit, it is off-hand hard to see how the vortex mode is established when the particle has no velocity at all. A preliminary study shows that the vortex is created by natural fluctuations leading to a thermally generated sound wave which smashes into the stationary sphere.⁵¹ This sound wave manifests itself by repeated successive collisions of the same solvent particle with the Brownian particle. This shows up in an unexpected positive structure in the force autocorrelation function, whose time integral determines the friction constant. This sound wave then leads to a temporary positive pressure on one side of the stationary object that relieves itself also by a vortex flow. Thus, the force autocorrelation function of a finite sized infinite mass particle also has a power law decay in time, just like the velocity autocorrelation function. Only for the infinite size and mass particle does this vortex flow make a vanishing contribution.

In that limit, the Stokes hydrodynamic model makes a prediction of the value of the friction constant. The proportionality constant in that

prediction depends on the nature of the boundary conditions between the fluid and the Brownian particle. For a perfectly elastic sphere the prediction is that the friction constant is 4π times the viscosity of the medium times the radius of the sphere. Curiously, by molecular dynamics, it was found at densities where the mean free path is small compared to the size of the stationary particle, and, hence, where hydrodynamics should be applicable, that the proportionality constant was 6π ; a value obtained only with sticking boundary conditions hydrodynamically. The implication is that boundary conditions are poorly understood from a molecular point of view, and that very likely in this case there must be, on a molecular scale, a boundary layer of solvent spheres around the stationary particle, whose net effect is to allow momentum transverse to the collisions also to be transferred, so as to justify the validity of the sticking boundary conditions.

In this connection, it should be pointed out that, nevertheless, the empirical observations for pure hard spheres are nearly in conformity with the Stokes-Einstein relation that uses 4π .⁴⁴ The significance, however, is unclear, since the Stokes-Einstein formula, which relates the diffusion coefficient with the viscosity, is not meant to apply for spheres of the same mass and size as the solvent.

(I) Burnett Coefficients

Although the ordinary transport coefficients were found to exist in three dimensions, the hydrodynamic and graph theoretical models predict divergence of the higher order transport coefficients. These transport coefficients, called Burnett coefficients, are concerned with wave length and gradient dependence. The wave length dependence,

characterized by the linear Burnett coefficients, accounts for the dependence of the transport coefficients on the rate at which the external field is applied, while the gradient dependence described by the non-linear Burnett coefficients accounts for the dependence on the amplitude of the external field. The linear Burnett coefficients can be evaluated by higher order autocorrelation functions. The first linear Burnett coefficient for diffusion, for example, can be expressed as the integral of an autocorrelation function of the velocity at four different times. Alternatively, the Einstein-like expression for this Burnett coefficient involves the mean of the fourth cumulant of the displacement of a particle. This can be easily programmed for molecular dynamics.

It was indeed shown that this Burnett diffusion in two dimensions, namely for hard disks, does diverge with one higher power in time than the ordinary diffusion coefficient; in agreement with the predictions of the models. The proportionality constant is, however, not in agreement with the prediction. Its density dependence is such that in the low density limit disagreement with the Chapman-Enskog expansion of the Boltzmann equation was found. Although these results have not been completely digested as yet, it is already clear that a power series expansions about the hydrodynamic limit in three dimensions diverges. How to formulate the higher order corrections to the Navier-Stokes equation is, hence, an open question. A clue, still preliminary, as to the reason for these divergences was obtained from a molecular dynamics study of the distribution in displacements. Since all the cumulants of this distribution higher than the first seem to be divergent, it appeared possible that the distribution would not be Gaussian in the long time limit. Indications are that this is the case.

It appears that the vortex mode restricts the large displacements of particles, because the flow pattern is such that these particles have velocity components that returns them to the origin. What was found, qualitatively consistent with this idea, was that the Gaussian distribution, previously thought valid, was only accurate for small displacements. The distribution had fewer large displacements than predicted by the Gaussian distribution.

(J) Depolarized Light

The trouble so far is that none of these long correlations have been directly observed experimentally. Besides the computer generated evidence, the only real manifestation of this vortex mode appears to be an indirect measurement, namely an enhanced diffusion coefficient at intermediate densities from what one would have predicted if the vortex correlations were left out.⁵² The lack of experimental evidence is not surprising in view of the smallness of the effect. The effect is largest for the diffusion coefficient; about 40% enhancement at intermediate densities. Indeed, the few accurate diffusion experiments at these densities and high temperatures are considerably more accurately predicted when interpreted by a hard sphere theory which includes the long tail correction, than by the Enskog theory, which ignores these correlations.

It would be desirable to obtain more evidence, and, therefore, an interpretation of a light scattering experiment was undertaken.⁵³ The line shape of depolarized light in fluid rare gases can be expressed as the Fourier transform of an autocorrelation function, namely, the induced dipole autocorrelation function. The idea was that the line shape close to the center of the band was a sensitive probe of the long time

correlations. Although the line shape near the center presents some experimental difficulties, it could potentially be obtained by special techniques. Furthermore, it must be realized that perhaps not all autocorrelation functions have long tails, so that the one appropriate to light scattering may not be the one to study.

Although this study was interesting in its own right, it failed to give evidence of long tails. The autocorrelation function calculation could explain the band shape, in so far as it is known experimentally, remarkably well. There is, so far, no experimental evidence of a long tail because the central shape has not yet been determined, and the computer results were largely negative that there would be one. It appears that only velocity dependent correlations have long tails, while only spatially dependent correlations, as the induced dipole autocorrelation, may behave normally in that respect. Much further work is required to understand both when long lasting correlations occur and what their consequences are, if they do.

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TABLE I

Correction to the van der Waals model
of the Helmholtz free energy, $-\Delta A/NkT$.

V/V_0	T	y_1	M.D.	O.F.	$C_V^E/2Nk$	O.C.T.
2.5	2.48	0.50	0.05	0.003	0.07	0.04
3.0	2.46	0.50	0.03	0.003	0.04	0.03
3.0	1.95	0.25	0.05	0.000	0.05	0.03
3.0	1.99	0.50	0.07	0.005	0.12	0.06
3.0	2.00	0.75	0.07	0.023	0.11	0.07
3.5	1.89	0.75	0.11	0.028	0.15	0.10
4.0	1.85	0.60	0.09	0.011	0.11	0.07

TABLE II

Thermodynamic properties of three mixtures
and also their excess properties on mixing at
constant temperature and pressure

(A)	$y_1 = 0.5$	$V/V_0 = 3.0$	$T = 1.99$	
	pv/NkT	U/NkT	G/NkT ^(a)	S/Nk
M.D.	2.53	-0.53	1.74	-0.75
O.F.	2.56	-0.40	1.84	-0.67
O.C.T.	2.53	-0.53	1.75	-0.75
excess	0.17 ^(b)	0.60	0.47	0.30 ^(c)
(B)	$y_1 = 0.8$	$V/V_0 = 3.0$	$T = 1.38$	
	pv/NkT	U/NkT	G/NkT	S/Nk
M.D.	1.31	-1.97	-0.61	-1.04
O.F.	1.34	-1.58	-0.50	-0.74
O.C.T. ^(d)	(1.35)1.29	(-1.89)-0.94	-0.61	-0.93
excess	0.11	0.76	0.53	0.34
(C)	$y_1 = 0.5$	$V/V_0 = 6.41$	$T = 1.41$	
	pv/NkT	U/NkT	G/NkT	S/Nk
M.D.	1.31	-0.41	-0.97	0.86
O.F.	1.37	-0.25	-0.84	0.96
O.C.T.	1.31	-0.41	-0.96	0.86
excess	0.27	0.97	0.42	0.82

$$(a) \quad G/NkT = A/NkT + pv/NkT - 1 + \ln \left(\sqrt{2} V/V_0 \right)$$

$$(b) \quad pv^E/NkT$$

$$(c) \quad S^E/Nk = U^E/NkT + p\Delta V/NkT - G^E/NkT$$

(d) Numbers in parenthesis are derived from the pair correlation function while all the other numbers are derived by differentiating the Helmholtz free energy. For the other two states, the two alternative methods give indistinguishable results.

TABLE III

Comparison of contributions to the virial
pressure for an 80% square-well mixture

(A) at $V/V_0 = 3$

T	P_{11}		P_{12}		P_{22}	
	M.D.	O.C.T.	M.D.	O.C.T.	M.D.	O.C.T.
∞	1.31	1.31	0.65	0.65	0.08	0.08
3.24	1.32	1.32	0.56	0.57	0.09	0.09
2.29	1.37	1.35	0.50	0.53	0.10	0.09
1.40	1.62	1.48	0.34	0.46	0.11	0.10

(B) at T of about 1.4

V/V_0	T	P_{11}		P_{12}		P_{22}	
		M.D.	O.C.T.	M.D.	O.C.T.	M.D.	O.C.T.
4	1.44	1.08	1.04	0.25	0.29	0.06	0.06
5	1.43	0.85	0.81	0.19	0.22	0.04	0.04
6	1.41	0.75	0.68	0.16	0.18	0.03	0.03

TABLE IV

Comparison of the compressibility factor
for an 80% square-well mixture at $V/V_0 = 3$

T	M.D.	O.C.T.g.	O.C.T.A.
3.24	2.30	2.295	2.302
2.29	2.00	1.989	2.004
1.60	-	1.536	1.570
1.38	1.31	1.293	1.347

TABLE V

Comparison of the excess internal energy, $-U/NkT$.

V/V_0	T	y	M.D.	O.F.	O.C.T.g.	O.C.T.A.
6.41	1.41	0.5	0.41	0.25	0.408	0.406
4	1.41	0.8	1.46	-	1.461	1.426
3	2.46	0.5	0.39	0.32	0.400	0.395
3	2.00	0.75	1.05	0.92	1.067	1.047
3	1.99	0.5	0.53	0.40	0.528	0.522
3	1.95	0.25	0.16	0.10	0.151	0.151
3	1.38	0.8	1.97	1.58	1.935	1.888
2.5	2.47	0.5	0.48	0.40	0.480	0.477

TABLE VI

Configurational excess heat capacity at constant volume.

(A) Variation with mole fraction at $V/V_0 = 3$ and T near 2

T	y_1	M.D. (a)	O.C.T.g	O.C.T.A
2.00	1.00	0.18		
2.00	0.75	0.23	0.264	0.272
1.99	0.50	0.24	0.193	0.196
1.95	0.25	0.09	0.070	0.074
2.00	0.00	0	0	0

(B) Other results

V/V_0	T	y_1	M.D.	O.C.T.g	O.C.T.A
3.5	1.89	0.75	0.31	0.305	0.284
4.0	1.85	0.60	0.24	0.246	0.244

(a) the heat capacity results are estimated to be accurate to $\pm 10\%$

(a)

(b)

(c)

(d)

(e)

(f)