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Monte Carlo Evaluation of the Partition Function for a Hard-Disk System*

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A Monte Carlo technique has been developed for evaluating the partition function of a hard-disk system which should be generalizable to other many-body integrals. Evaluating the partition function directly, and hence the free energy per particle, instead of simulating the system allows much smaller systems to be used as realistic samples of an infinite system since a canonical ensemble of such systems is actually sampled. This eliminates the metastable-state problem that tends to lock simulated systems in one phase or another. The free energy has been evaluated for a 16-particle system with periodic boundary conditions for $0 \leq \rho \leq 0.9$ with ρ = density/close-packed density. The free energy is below that of a free-volume calculation which assumes crystallization for $\rho \leq 0.79$ and equal to it for higher densities. At $\rho = 0.8$ the free-volume equation can be extrapolated to $N = \infty$ and gives $A(0.8)/NkT = 4.01 \pm 0.04$, which compares well with the 3.96 ± 0.01 which Ree and Hoover obtained by integrating the pressure curve. The pressure in the phase-change region can also be extrapolated to give $PV_0/NkT = 7.6$, which compares well with the Alder–Wainwright result of 7.72. The phase-change region, the only part which cannot be easily extrapolated, is $1.25 \leq V/V_0 \leq 1.28$ for 16 particles, which is about the correct density but only about 60% of the width of theirs ($1.266 \leq V/V_0 \leq 1.312$) for 870 particles because of a combination of $1/N$ effects and smoothing in fitting to the A/NkT data.

I. INTRODUCTION

It just does not seem right that 870 particles and about ten million collisions for each density[1] should be required to see a phase change in a hard-disk system which can have at most nearest-neighbor interactions and for which the crystal unit cell would contain only one particle. The interesting feature of this phase change is that it occurs in a system with no attractive interactions which implies that it can only be due to the packing geometry required to have that many particles at the given density, and that it occurs in an easily visualizable two-dimensional system. Unfortunately such a large number of particles and collisions destroys a good deal of this simplicity, and one wonders if they are really needed. Indeed there is some evidence available that they are not. No signs of first-order phase transition are evident from the standard molecular-dynamics and Monte Carlo studies of hard-disk systems of 4 and 12 particles, yet a two-particle system with periodic boundary conditions can be shown to have a van der Waals-like loop at about the density and pressure where the larger systems have a first-order transition, and possibly even more telling for a calculation of the type made here, an evaluation of the configurational integral of a periodic system of four hard parallel squares shows that it also has a first-order phase change.[2] Unfortunately these systems are so small and specialized that one cannot be sure that the results are not simply due to having very small systems. However, if it were possible to find this result in a 16-particle system with a method that in no way, other than machine-time considerations, depended on the 16-particle limitation, the entire system could be modeled with coins and the connection between small-system and large-system results should be fairly easy to see.

The problem in doing this normally stems from the impossibility of having a two-phase region in such a small system. This is not a problem here because the system is not simulated but rather the configurational integral is calculated from the results of independent trials with gas and crystal states entering into these trials according to their relative abundances. One would expect of course that some dependence on N, the number of particles, would certainly be present in so small a system, making the pressure, free energy, and phase-change region different from those observed in the $N \rightarrow \infty$ limit, and indeed this is the case. Fortunately, though, the simplicity of such a small system enables one to deduce in the free-volume limit, where crystallization has taken place, the explicit form of the N dependence so that values on the crystal side of the phase-change region for the 16-particle system can be extrapolated to the $N \rightarrow \infty$ limit, giving a free energy $A/NkT = -(\ln Z)/N$, which is calculated directly in this method, at $\rho/\rho_{cp} = 0.8$ of 4.01 ± 0.04 for the infinite system deduced from the 16-particle system. This compares well with the value 3.96 ± 0.01 which Ree and Hoover obtained by integrating the pressure curve for the $N \rightarrow \infty$ limit.[3] The pressure involves a derivative of the free-energy curve and is therefore subject to smoothing errors in the polynomial fit to the A/NkT data. However it still extrapolates in $N\rightarrow\infty$ limit to $PV_0/NkT=7.6$, which is close to the Alder–Wainwright result of 7.72. The phase-change region on the other hand does not extrapolate and is therefore subject to both $1/N$ errors and smoothing from the polynomial fit and it gives $1.24\leq V/V_0\leq 1.28$, which is in the correct location but only about 60% of the width of the Alder–Wainwright result of $1.266\leq V/V_0\leq 1.312$.

The configurational part of the classical canonical partition function is

$$Z(N, V, T)=(1/N!)\int_V\int_V\cdots \times\int_V d\vec{q}_1\cdots d\vec{q}_N e^{-V(\vec{q}_1\cdots\vec{q}_N)/kT} . \quad (1)$$

The number of dimensions tied together in the integral suggests the Monte Carlo method as the cheapest way to evaluate it. The difficulty is that for a dense system of particles with hard cores virtually every random choice of the variables $\vec{q}_1, \ldots, \vec{q}_N$ will contain at least two q's sufficiently close that they are within the hard-core radius. This means that virtually all choices give zero as the value of the integrand and that the machine's time is almost all spent in generating q's which do not contribute to the integral.

For this reason, the integral itself has not normally been evaluated. Instead the system has been simulated by allowing N particles to move in the volume V under the influence of the potential $V(\vec{q}_1, \ldots, \vec{q}_N)$ either in a very direct fashion by solving stepwise the equations of motion, as in the molecular-dynamics method, or indirectly by moving a particle randomly to a new location resulting in a change of potential ΔV, and then accepting the new location as a new position for the particle or rejecting it and accepting the old position according to the Boltzmann probability $e^{-\Delta V/kT}$, as in the Monte Carlo method.[4] Thermodynamic averages are then calculated by averaging over all of the sets of $\vec{q}_1, \ldots, \vec{q}_N$ occurring after equilibrium has been reached. Both of these methods are similar to an experiment in which a system is prepared at time t_0 and its equilibrium properties determined by averaging between times t_1 and t_2 after it has hopefully reached equilibrium. There are two difficulties: First, the details of $V(\vec{q}_1, \ldots, \vec{q}_N)$ are needed to determine the values of $\vec{q}_1, \ldots, \vec{q}_N$ entering into the averages, which means that one cannot compare the results of any two potentials V_A and V_B by directly calculating the difference, but must determine each with its random errors independently to high enough accuracy to compare them. Second, if metastable states are present, there is a danger that short times and small numbers of particles will find themselves locked in such states so that the system never really goes to equilibrium.

The method proposed here goes back to evaluating the integral itself in a Monte Carlo fashion but with a biased method for picking the random variables so that an acceptable fraction of the trial choices contributes to the integral. Although none are made here, this means that comparisons between $V_A(\vec{q}_1, \ldots \vec{q}_N)$ and $V_B(\vec{q}_1, \ldots, \vec{q}_N)$ can be made directly if the bias is such as to satisfy the more restrictive of the two since the integral evaluated could be, for example,

$$Z_p(N, V, T)=(1/N!)\int_V\int_V\cdots \times\int_V d\vec{q}_1\cdots d\vec{q}_N\left(e^{V_A/kT}-e^{V_B/kT}\right), \quad (2)$$

where the difference is all that appears in the integrand. The metastable-state problem does not enter at all since the sets of choices are totally random with respect to each other, which is what makes it possible to use very small numbers of particles and fewer trials with this method in regions where metastable states occur than with the conventional methods. Unfortunately these advantages are not free. The biased selection method means that some choices of $\vec{q}_1, \ldots, \vec{q}_N$ are weighted much more heavily than others, which introduces extra fluctuations into the value of the integrand and thereby increases the number of trials needed. In addition the biased selection method usually results in acceptable choices of $\vec{q}_1, \ldots, \vec{q}_N$ in the higher-density region for only about 10–20% of the trials (the percentage can be increased but also increases the dispersions in the weightings) so that in some ways the method is inherently wasteful. More seriously, a midpoint trapezoidal-rule estimate of the integral is calculated rather than the integral itself which introduces its error superimposed on the random error which must be extrapolated away. Despite this, the advantages of smaller numbers of particles and the conceptual attractiveness in calculating the integral itself rather than thermodynamic averages probably outweigh the disadvantages.

II. GENERAL METHOD

The area V of a hard-disk system is taken to be an equal-sided 60° parallelogram with periodic boundary conditions along the directions of the sides. A mesh is superimposed on V such that it is divided into N_s hexagonal regions with a mesh point numbered from 1 to N_s in the center of each region, where the number is made to correspond to an address in which information can be stored about the mesh point. The variables $\vec{q}_1, \ldots, \vec{q}_N$ are then restricted to the mesh points so that the sum

$$Z(N_s, N, V) = \frac{1}{N!}\left(\frac{V}{N_s}\right)^N \times \sum_{\vec{q}_1=1}^{N_s} \cdots \sum_{\vec{q}_N=1}^{N_s} e^{-V(\vec{q}_1, \ldots, \vec{q}_N)/kT}, \tag{3}$$

which is independent of temperature because of the zero or infinite nature of the hard-disk potential, is a midpoint trapezoidal-rule approximation to the configurational integral given by

$$Z(N, V) = \lim_{N_s \to \infty} Z(N_s, N, V) \,. \tag{4}$$

This sum is not actually evaluated directly, instead the number n_p of different sets of $\{\vec{q}_1, \ldots, \vec{q}_N\}$ with the q's in any order is estimated by comparing an observed probability of finding such a set when the choices are made in a biased manner with the probability of finding any one such set which can be calculated from the number of choices available before each $\vec{q}_i$ was picked. The number n_p of these sets then times the number of permutations $N!$ of each set is just the value of the sums in the equation for $Z(N_s, N, V)$ so that

$$Z(N_s, N, V) = n_p V^N / N_s^N \,. \tag{5}$$

In order to decide how to bias the random selection process it pays to look at the 16-particle system, or equivalently at 16 pennies on a piece of cardboard. For low densities, the overriding criterion is simply that two pennies cannot be placed on top of each other, therefore we eliminate any such possibility from the possible choices of $\{\vec{q}_i\}$ and then note the number left in the set and use it to calculate the bias introduced. At higher densities it makes a tremendous difference in the calculated bias which order a given set of q's is introduced in, with all on one side first giving a tremendously smaller bias than alternatively on one side and than the other, so we permute them and average the bias for a given set of q's. Then at the highest densities the pennies almost always form a crystal. Therefore start with crystal locations but also add all other possibilities to form a sequence which converges to n_p in general quite rapidly at high densities, where the crystal locations exhaust the possibilities, and somewhat slower at lower densities, where gas configurations can be observed to come in as the relative numbers from the crystal locations decrease relative to those from the random locations.

III. LOW AND MEDIUM DENSITIES

For low densities the biased selection method is as follows: A trial value of $\vec{q}_1$ is selected from the set E of available mesh points $E_1 = N_s$. Then each point within a radius d corresponding to the diameter of a disk is removed from the set E by checking the location associated with each point and storing a number in it, if it does not already have one, and subtracting one from the number of available mesh points each time a point without a number is found, leading to E_2, the number of mesh points available for the choice of $\vec{q}_2$, which is then chosen from the set E of remaining points, and again the appropriate points are removed from E, leading to E_3 points from which the third q can be chosen, and so on. The number stored to indicate that the point is no longer in E could be merely a 1, but in practice it was convenient to make it the number of the highest remaining available point so that random numbers picked from 1 to E_i could be redirected to that point if a point not in E was chosen randomly, leading to an equal probability of picking any point in the set with no need to discard any random numbers. The probability w_t then of having made a choice $\vec{q}_1, \ldots, \vec{q}_N$ in the specified order in a given trial is given by

$$w_t = \prod_{i=1}^{N} \frac{1}{E_i} \,, \tag{6}$$

since at each step i the probability of having chosen the $\vec{q}_i$ that was picked is just $1/E_i$. Note that a trial set of q's might manage to box themselves in, so that after the rth choice it is impossible to find q_{r+1} without two q's being closer than d. This leads to $E_{r+1} = 0$ and to $1/w_t = 0$ or to infinite w_t.

The probability $P(w_t)dw_t$ of finding a value of w_t in the range dw_t for a given trial and finite w_t is just the product $w_t n(w_t) dw_t$, where $n(w_t)dw_t$ is the number of sets of $\vec{q}_1, \ldots, \vec{q}_N$ with the order specified, which give rise to values w_t in the range dw_t when they are chosen. This leads to $n(w)dw = P(w)(1/w)dw$ which needs to be integrated over all finite values of w to find the total number of nonoverlapping q sets in the system. Fortunately infinite w's result from $1/w_t = 0$ and these imply that $n(\infty) = 0$, which is just what is needed to extend the integral to all values of w, so that

$$n_p N! = \int_0^\infty \frac{P(w)}{w}\, dw = \left\langle \frac{1}{w} \right\rangle = \lim_{N_t \to \infty} \frac{1}{N_t} \sum_{t=1}^{N_t} \frac{1}{w_t} \,, \tag{7}$$

where the $N!$ accounts for the possible permutations of each set and N_t is the total number of trials made. Terms appear in the sum with the probability $P(w_t)$ owing to the fact that that is the definition of $P(w)$.

At low densities $(0 - 0.4\rho_{cp})$, the biased selection method leads to almost every trial giving a finite value for w_t and also leads to relatively small fluctuations in the value of w_t so that the above is sufficient. At higher densities $(0.4\rho_{cp} - 0.7\rho_{cp})$ w_t begins to vary drastically. In addition only about one trial in 10 or 20 may yield a finite value for w_t. The reason for the large variations is fairly easy to see. Suppose that there were only one set of nonoverlapping q's in the system. Obviously they can be picked in any order and sometimes might be picked so that the first value is from one side of the system, the second from the other, etc., so that each time many points are removed from the system, making the first few E_i's decrease rather rapidly. Another time the same values of q might be picked in an order such that the first, second, third, etc., choices are almost nearest neighbors, and the E_i's have only a few points removed from them after each choice, leading to a much smaller value for w_t than in the first case. This was not a problem at low densities because the disks were almost always far enough apart that all of the points within a radius d were removed after each choice. It is a problem at higher densities because a large fraction of the points within the radius d may or may not have been removed from the set by previous choices so that the order of making these choices becomes important. At this point it pays to save the values of any ordered set $\vec{q}_1, \ldots, \vec{q}_N$ which is picked in the biased method and to permute the set, making, for example, $\vec{q}_5' = \vec{q}_1$, $\vec{q}_1' = \vec{q}_7$, etc. These are then put into the system in the new order in order to find the new E_i's from which w_t' is calculated for a number of such permutations and then averaged to give $\bar{w} = \langle w_t \rangle_p$ which is the average probability of the set $\vec{q}_1, \ldots, \vec{q}_N$ having been chosen in any order. The probability of getting a specified value of $\bar{w}$ in a given trial is proportional to the number $m(\bar{w})$ of such sets with the appropriate size $\bar{w}$ times $N!$ to convert the average into the total probability independent of order. Therefore, we have

$$m(\bar{w}) N!\, d\bar{w} = P(\bar{w})(1/\bar{w})\, d\bar{w} , \tag{8}$$

and the total number of sets is given by

$$n_p N! = \int_0^\infty \frac{P(\bar{w})}{\bar{w}}\, d\bar{w} = \left\langle \frac{1}{\bar{w}} \right\rangle = \lim_{N_t \to \infty} \frac{1}{N_t} \sum_{t=1}^{N_t} \frac{1}{\bar{w}_t} , \tag{9}$$

where it should be noted that w_t is first averaged over the permutations of the q's chosen on the tth trial to form $\bar{w}_t$ and that $1/\bar{w}$ is then averaged over the N_t trials made. A specific example of the method is shown in the Appendix.

Since the q's are chosen one at a time and in a random manner from those possible, the information about N particles in V is also information about $M < N$ particles in V so that, except for the mild dependence on the total number of particles present in the quantities calculated, a single run finds these for all densities up to a maximum determined by the failure of the method to yield any possible nonoverlapping q arrangements. The inevitability of this failure is easy to see since the biased selection method employed above is very similar to randomly throwing things in a closet, and if one really wants to get to high densities a certain amount of planning is needed.

IV. HIGH DENSITIES

For densities greater than $0.7\rho_{cp}$ a somewhat less random selection method is needed. The first position $\vec{q}_1$ could be taken as any of the N_s points since it specifies the origin of the system. Then the second choice $\vec{q}_2$ could be made from any of the points within rings of width r_a and diameters equal to the nearest-, next-nearest, etc., neighbor distances that a set of particles equally spaced in V would have. The second choice having specified the orientation of the system, the third, fourth, etc., choices of $\vec{q}_i$ would then be made from any of the points within circles of radius r_a centered about the points which would be occupied by equally spaced particles with one at $\vec{q}_1$ and another in the circle specified by $\vec{q}_2$. The beauty of this method is that it guarantees finding a set $\vec{q}_1, \ldots, \vec{q}_N$, since by making r_a sufficiently small we can limit the possible choices to those which would allow the system to fill even for the case of the close-packed density itself. One more addition, however, is necessary. It is now possible to divide the possible sets of $\vec{q}_1, \ldots, \vec{q}_N$ for which no two are closer than d into the categories all chosen as specified above, the last chosen from the mesh points which cannot be reached in this way (from outside of all of the circles of radius r_a), the last two from mesh points outside of the circles of radius r_a, etc., with a bit of care needed for the choice of q_2 outside of the mesh points of the above method since it must be not only outside of the circles but also outside of the rings formed by rotating the circles. The probability of having chosen a single set of q's in the order specified is still given by Eq. (6), with the E_i's not the number of empty spaces in the space V, but rather the number of spaces available for choosing in the manner specified. The number of different permutations of the q's is now subject to the constraint that $N - I$ of them be chosen from the first region and I from the second, so that Eq. (7) becomes

$$n_I (N-I)!\, I! = \lim_{N_t \to \infty} \frac{1}{N_t} \sum_{t=1}^{N_t} \frac{1}{w_t} \quad (I = 0, 1, \ldots, N), \tag{10}$$

$$n_p = \sum_{I=0}^{N} n_I , \tag{11}$$

where again it is possible to average over permutations so that w goes to $\bar{w}$ as in Eq. (9).

The n_p calculated in this way is totally independent of the size assumed for r_a, since any possible arrangement which does not appear in one of the categories of q sets will appear in another and this has been utilized for checking that the above equations work for low densities. The size of r_a, however, does affect the relative numbers of particles present in the various categories. For example, if r_a is made sufficiently large, there are no points which are not included in the first category, which becomes equivalent to the biased selection method used for low densities. The game is to make r_a sufficiently large that for a given density most of n_p comes from the first few categories with a reasonable fraction of the trials giving nonoverlapping q sets.

An approximation leading to a small systematic error for high densities must be mentioned here. In principle the second particle is put into one of the rings and then the circles are formed for the rest of the particles so that all orientations are automatically included. In practice, the first particle was placed at the center of the system, the circles were formed about the lattice sites determined by it and its periodic repetitions, and the second particle was also placed in one of these circles. The resulting n_p was then multiplied by the ratio of the number of points in the rings to the number in the circles on the assumption that the number of possible configurations would be the same for all orientations of the system. This approximation should be fairly good even at most crystal densities since there are almost no configurations with particles on the lattice sites, but rather most have the particles displaced one way or the other. For orientations other than the one used the particles will need to be closer together in some directions but can be further apart in others so that there should still be about the same total number of configurations. For a close-packed system, however, this must break down, and hence the approximation used introduces a small error. The result is that at extremely high densities A/NkT as calculated above will go as $[(2N-3)/N]\ln(\rho^{-1/2}-1)$ instead of going as the correct $[(2N-2)/N]\ln(\rho^{-1/2}-1)$. This point will be further discussed in Sec. V.

V. FREE-VOLUME LIMIT

At sufficiently high densities it is possible to deduce the results of the high-density method without using a computer. Let b be the distance between the particles of diameter d when each is placed in a hexagonal pattern equidistant from its neighbors, and let V_p be the area of a hexagon circumscribed about one of the disks. Then we can find the relations

$$N_s = (V/V_p)d^2 , \tag{12}$$

$$(N_s^{1/2} - dN^{1/2}) = bN^{1/2} , \tag{13}$$

$$\rho = NV_p/V = V_0/V , \tag{14}$$

so that the relation between b and d is

$$b = [(V/NV_p)^{1/2} - 1]d = (\rho^{-1/2} - 1)d . \tag{15}$$

Now imagine putting the particles into the system with the high-density selection method: The first q is chosen anywhere, $E_1 = N_s$. The second is chosen from any of the concentric rings about the first q corresponding to the appropriate nearest-neighbor, next-nearest-neighbor, etc., distances containing $c_1\,db$ points, $E_2 = c_1\,db$. The third q is then chosen from any of the remaining $N-2$ circles centered about the equidistant particle points containing $c_2 b^2$ points each, $E_3 = (N-2)c_2 b^2$. The fourth q is chosen from $N-3$ circles, etc., with the remaining q's being chosen from the appropriate number of circles so that we find for $\langle 1/w\rangle$

$$\langle 1/w\rangle = N_s\, c_1 db\, (N-2)!\, (c_2 b^2)^{N-2} , \tag{16}$$

which gives n_p from Eq. (7) as

$$n_p = N_s c_1 c_2^{N-2} db^{2N-3} N^{-1}(N-1)^{-1} \tag{17}$$

and Z from Eq. (5) as

$$\begin{aligned} Z(N_s, N, V) &= V^N c_1 c_2^{N-2} db^{2N-3} N^{-1}(N-1)^{-1} N_s^{1-N} \\ &= V_p^N (V/NV_p) c_1 c_2^{N-2} (b/d)^{2N-3} (N-1)^{-1} \\ &= V_p^N \rho^{-1} c_1 c_2^{N-2} (\rho^{-1/2} - 1)^{2N-3} (N-1)^{-1} , \end{aligned} \tag{18}$$

and we find that the free energy per particle $A/NkT = -(\ln Z)/N$ is given by

$$A/NkT = C_N + \frac{\ln\rho}{N} - \frac{2N-3}{N}\ln(\rho^{-1/2} - 1), \tag{19}$$

with

$$C_N = -\ln V_p - \frac{\ln c_1}{N} - \frac{(N-2)(\ln c_2)}{N} + \frac{\ln(N-1)}{N} . \tag{20}$$

Equation (19) contains the same assumption as the numerical work that the second particle can occupy any of the mesh points at the correct distances from the central particle. As discussed at the end of Sec. IV, this should be reasonable for most densities, since only a slight adjustment of already displaced particles is required to account for the fact that the periodic repetitions of the system do not quite fit the original system, which should not significantly change the number of choices available before each step. At the very highest densities, however, the second particle is also limited to the circles owing to the fact that these adjustments become impossible, which changes the coefficient of $\ln(\rho^{-1/2} - 1)$ in Eq. (19) from $(2N-3)/N$ to $(2N-2)/N$. This change probably occurs gradually and as mentioned at the end of Sec. IV the numerical work was done in such a way that it will go as Eq. (19) even at the highest densities.

As $N \to \infty$, Eq. (19) becomes the familiar free-volume result, but more importantly for the finite N it tells us what A/NkT should look like in the *crystal* region. The reason that this is relevant for the crystal region and not for the gas is because for a crystal the vast bulk of the possible configurations really do have the particles spaced as in the derivation, while for a gas the configurations with all of the particles within b of a lattice site make up only a small proportion of the total number of configurations possible.

VI. TRAPEZOIDAL-RULE ERROR

In a lowest approximation each particle can be treated as though it were free to move inside a circle of radius $R(N/V)$ which is determined by the positions of the other particles so that

$$Z(N,\ V) = \left(2\pi \int_0^{R(N,\ V)} r\,dr\right)^N = \pi^N R(N,\ V)^{2N}. \tag{21}$$

Two sources of error are introduced when the q's are constrained to be on the N_s mesh points. In the first place, the other particles are not where they want to be but are displaced from their natural positions by an amount proportional to the distance between mesh points or $1/d$, where d is the diameter of a disk in mesh points. This is a continuous sort of error in that the particles can place themselves better and better as d becomes larger so that $R(d,\ N,\ V)$ is given by $R(N,\ V)$ plus an error term $\epsilon(N,\ V)/d$, which gives rise to

$$Z(1/d,\ N,\ V) = \pi^N [R(N,\ V) + \epsilon(N,\ V)/d]^{2N}, \tag{22}$$

and the free energy per particle is given by

$$\begin{aligned} A/NkT &= -2\ln[R(N,\ V) + \epsilon(N,\ V)/d] - \ln\pi \\ &= -2\ln R(N,\ V) - \ln\pi - \frac{2[\epsilon(N,\ V)/R(N,\ V)]}{d}, \end{aligned} \tag{23}$$

so that a linear dependence on $1/d$ would be expected from this error source. The other source of error comes after $R(N,\ V)$ has been determined. The integral in Eq. (21) still needs to be done and is done by trapezoidal rule and hence depends on the number of mesh points within the circle of radius $R(N,\ V)$. Unfortunately the ratio of the number of points times the area of the hexagon which they represent compared to the area of a circle of a given radius does not become continuously better as d increases, but rather jumps from too large to too small and back again many times as d increases. It is also far from obvious that the area of interest is exactly a circle, so that a correction for this would be extremely difficult with the result that a certain amount of jumpiness is expected to be superimposed on the general linear trend of A/NkT when plotted as a function of $1/d$.

VII. RESULTS FOR HARD DISKS

The area V of the system is a 60° equal-sided parallelogram with periodic boundary conditions along the directions of the sides corresponding to a multiple of the expected unit cell for the crystal phase. Extreme accuracy in Z, whose logarithm divided by N determines A/NkT, is not needed, only its order of magnitude. The rule adopted here was to find Z to within a standard deviation, which was determined by comparing independent trial runs, of $\sigma \le \frac{1}{2}Z$ so that two standard deviations of error would be required to change Z's order of magnitude. This results in a standard deviation for A/NkT of about 0.03 and is sort of the minimum accuracy possible. At low and medium densities, where the selection method gave Z for all N's up to a maximum, N values between 12 and 20 were used as good approximations to the $N = 16$ results. At high densities, $\rho \ge 0.7$, N was fixed at 16 and the area of the system varied to give different densities. At high densities as many different values of the disk diameter d as possible within the constraints that d and the side of the system be integral were used for each density and in addition all possible densities for $d = 12$ were used. In the middle-density region d values of 4, 6, and 12 were used with the substitution of 10 for 12 and then 8 for 12 at the extreme low-density end.

Since Z itself is obtained directly one should not be surprised to find that relatively few sets of $\{\vec{q}_1, \ldots, \vec{q}_N\}$ are needed to give the desired accuracy. For example, if one was actually doing a straightforward Monte Carlo evaluation of the integral in Eq. (1), only four such sets would be needed to establish the probability of finding a set of nonoverlapping q's to within 50% and hence Z to this accuracy. The only additional source of fluctuations here occurs in w_t from Eq. (6) which we can almost determine without a computer.

For example, at low densities the E_i's of Eq. (6) are almost always simply the total number of mesh points N_s minus the number of mesh points in i circles of radius l with a small correction to determine the probability of choosing two $\vec{q}$'s sufficiently close that some of the full circle about the second has already been removed from the set by the first. The constancy of this plus the fact that Z is needed only to extremely low accuracy implies that only about 20 to 50 independent trial choices were needed at these densities. Even for the highest densities obtainable by the low- and medium-density method, only few sets of q's are needed, although averaging over the permutations of each set is essential, owing to the fact that the E_i's are still relatively large with only small dispersions introduced by the exact positions of the

$\{\vec{q}_1, \ldots, \vec{q}_N\}$ sets. Unfortunately a fair number of independent trials, on the order of 250 to 1000, is needed just to find 20 or so of these sets, which makes these densities much more time consuming.

With the high-density method, the E_i's become smaller while the frequency of finding a set $\{\vec{q}_1, \ldots, \vec{q}_N\}$ becomes larger. Fluctuations in the number of points comparable to those with the medium-density method here make up a larger fraction of E_i, so that the smaller the E_i is originally the larger will be the fluctuations, which means that a trade off occurs in determining the size of the first region, such that a smaller region gives rise to more sets of $\vec{q}$'s but also to larger fluctuations. A success rate of about 10–20% was found to be about the best combination, and about 50 $\{\vec{q}_1, \ldots, \vec{q}_N\}$ sets were then needed to find Z to the desired accuracy. The final result of about 5 or 6 h on a CDC 6400 computer was 146 such points. These were then put in the form $A(1/d, \rho)/NkT - A_i(\rho)/NkT$, where $A_i(\rho)$ is the free energy of an ideal gas, given by

$$\frac{A_i}{NkT} = -\frac{\ln(V^N/N!)}{N}$$

$$= -\ln\left(\frac{V}{NV_p}\right) - \ln V_p - \left(\ln N - \frac{\ln N!}{N}\right) \tag{24}$$

$$= \ln\rho - \ln V_p - 1\ , \tag{25}$$

where the last is the $N \to \infty$ limit used in the comparison. It should be noted that the $\ln V_p$ is just what is needed to cancel that left over from Eq. (20), and also that the difference between the bracketed term for $N = 16$ and for $N \to \infty$ is the difference to be expected between A/NkT and A_i/NkT in the limit as $\rho \to 0$; this difference is 0.144. The points were then least-squares fitted to the 14 constants of a two-dimensional polynomial of sixth

TABLE I. The actual values of A_c/NkT calculated along with

$$A(\rho,d) = (0.144 - 0.06/d) + (-0.236 + 26.71/d)\rho + (31.610 - 301.46/d)\rho^2 + (-146.251 + 1331.06/d)\rho^3 + (309.984 - 2775.03/d)\rho^4 + (-293.429 + 2740.66/d)\rho^5 + (105.345 - 1042.80/d)\rho^6,$$

which was least-squares fitted to these values. All of the values used in this fitting for densities greater than 0.4 are given here along with a sample of the values for lower densities.

ρ	d	A_c/NkT	A/NkT	ρ	d	A_c/NkT	A/NkT	ρ	d	A_c/NkT	A/NkT
0	∞	0.144	0.144	0.4286	6	1.10	1.16	0.6000	6	1.81	1.93
0.1000	4	0.37	0.34	0.4325	10	1.24	1.19	0.6168	4	1.99	1.95
0.1000	6	0.37	0.33	0.4354	4	1.17	1.17	0.6205	4	2.01	1.97
0.1500	4	0.42	0.43	0.4400	4	1.21	1.18	0.6205	12	2.13	2.12
0.1500	6	0.41	0.44	0.4400	6	1.17	1.20	0.6400	4	2.11	2.08
0.1938	8	0.55	0.54	0.4432	4	1.24	1.19	0.6400	6	2.03	2.16
0.2000	4	0.50	0.51	0.4542	10	1.32	1.27	0.6421	6	2.12	2.18
0.2000	6	0.49	0.54	0.4550	12	1.30	1.28	0.6421	12	2.32	2.27
0.2076	8	0.57	0.57	0.4709	6	1.29	1.32	0.6531	4	2.20	2.15
0.2163	10	0.64	0.60	0.4709	12	1.38	1.34	0.6619	12	2.49	2.40
0.2245	4	0.61	0.56	0.4717	4	1.29	1.30	0.6800	6	2.30	2.43
0.2245	6	0.60	0.60	0.4800	4	1.35	1.33	0.6849	6	2.42	2.46
0.2352	8	0.63	0.64	0.4800	6	1.30	1.35	0.6849	12	2.67	2.57
0.2379	10	0.68	0.65	0.4875	4	1.40	1.36	0.7090	4	2.54	2.50
0.2449	4	0.65	0.61	0.4964	12	1.47	1.45	0.7090	8	2.73	2.69
0.2449	6	0.63	0.64	0.5079	4	1.44	1.44	0.7090	12	2.85	2.76
0.2491	8	0.66	0.67	0.5137	6	1.45	1.50	0.7347	6	2.80	2.82
0.3028	10	0.83	0.82	0.5137	12	1.55	1.53	0.7347	9	2.85	2.91
0.3061	4	0.78	0.76	0.5200	4	1.51	1.49	0.7347	12	2.96	2.96
0.3061	6	0.76	0.79	0.5200	6	1.45	1.51	0.7617	12	3.16	3.19
0.3460	10	0.95	0.92	0.5319	4	1.58	1.54	0.7901	4	3.01	3.02
0.3469	4	0.88	0.88	0.5387	12	1.65	1.65	0.7901	6	3.26	3.22
0.3469	6	0.86	0.90	0.5442	4	1.60	1.59	0.7901	8	3.37	3.33
0.3673	4	0.94	0.94	0.5565	6	1.63	1.70	0.7901	12	3.45	3.43
0.3676	10	1.02	0.98	0.5565	12	1.75	1.75	0.8202	12	3.63	3.70
0.3893	10	1.08	1.05	0.5600	4	1.69	1.66	0.8521	6	3.62	3.64
0.4082	4	1.05	1.07	0.5600	6	1.62	1.71	0.8521	12	3.92	3.99
0.4082	6	1.03	1.09	0.5762	4	1.79	1.74	0.8521	15	4.09	4.06
0.4109	10	1.16	1.12	0.5791	12	1.87	1.87	0.8858	4	3.28	3.30
0.4137	12	1.16	1.13	0.5805	4	1.79	1.76	0.8858	8	4.12	4.05
0.4281	6	1.15	1.16	0.5993	6	1.85	1.92	0.8858	12	4.32	4.30
0.4281	12	1.22	1.18	0.5993	12	2.01	1.99	0.8858	16	4.44	4.43
0.4286	4	1.12	1.14	0.6000	4	1.88	1.86	0.8858	32	4.58	4.61

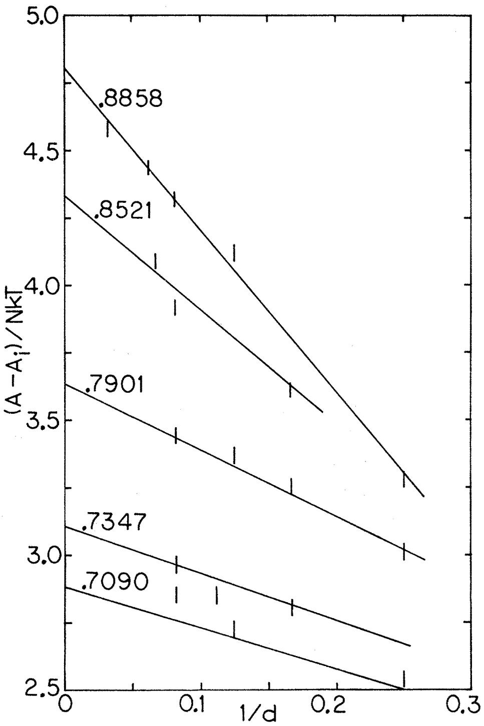

FIG. 1. Free energy per particle A/NkT for the 16-particle system minus that for an equivalent infinite-particle ideal gas A_i/NkT vs $1/d$, the reciprocal of the number of mesh points across a particle. This enables one to see the extrapolating away of the mesh. The lines are from a polynomial fitted to the 146 data points, while the slashes represent those high-density data points with ρ's, given by the numbers, for which there were more than two points at the same density.

degree in ρ and linear in $1/d$ subject to the constraint of being 0.144 for $\rho = 0$, $1/d = 0$. Most of the points are compared to the fit in Table I, and the result in the high-density region is shown in Fig. 1 where the slashes are those points with more than two points at the same density, and the lines in the figure are from the fit. The polynomial has a standard deviation from the points to which it was fitted of $\sigma = 0.04$ which is due in part to the difficulty of fitting an entire curve by a single polynomial, in part to the deviations of the points themselves, and in part to the jumpiness mentioned in Sec. VI. Extrapolated to $1/d = 0$, the curve fit gives

$$A(\rho)/NkT - A_i(\rho)/NkT = 0.144 - 0.236\rho + 31.610\rho^2 - 146.251\rho^3 + 309.984\rho^4 - 293.429\rho^5 + 105.345\rho^6 \qquad (26)$$

valid for $0 \leq \rho \leq 0.9$ with $\sigma \approx 0.04$, where the deviation quoted is that of the polynomial from the points to which it was fitted, which in view of the extrapolation seen in Fig. 1 and of the strange behavior expected near the phase change is probably as good an estimate of the accuracy of the curve as any other. This curve is shown in Fig. 2 along with the curve based on Eq. (19) for the free-volume limit. The constant C_{16} for that equation was found by the requirement that the two curves agree for the highest density calculated, $\rho = 0.8858$, which gives $C_{16} = -1.35$. The impressive part is that these two curves agree almost exactly for densities greater than $\rho = 0.79$. This agreement is shown even more clearly in Fig. 3 where the difference between the two curves is plotted on an expanded scale. The difference goes to zero at $\rho = 0.79$ and within the error of the polynomial stays there or rather oscillates in the typical manner of a polynomial trying to adapt to a new curve.

The free energy A/NkT calculated by Ree and Hoover in the $N \to \infty$ limit by integrating the pressure curve[3] is also shown in Fig. 2 as the open circles. For low densities the 16-particle curve is above their points by about 0.14 as was anticipated in the remarks below Eq. (24). For high densities the 16-particle results are *below* their points which might seem surprising at first, but

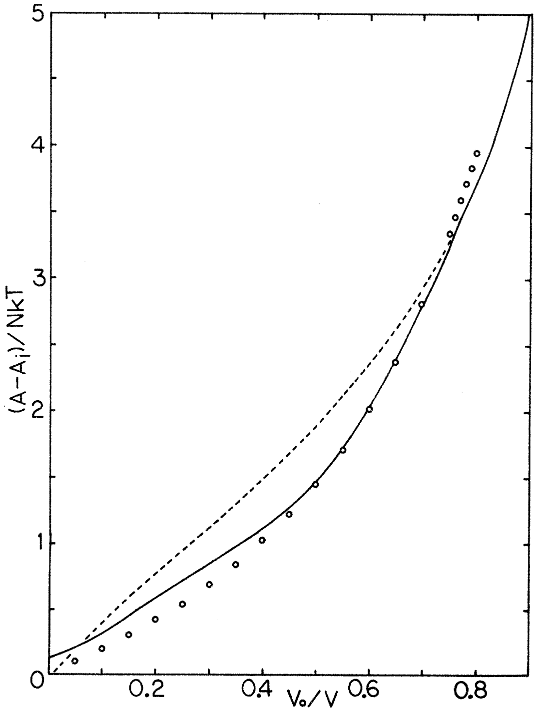

FIG. 2. Free energy per particle minus that of an ideal gas, $A/NkT - A_i/NkT$ vs $\rho = V_0/V$. Solid line, polynomial fit to the data extrapolated to $1/d = 0$; dashed line, the 16-particle free-volume limit [Eq. (19)] with $C_{16} = -1.35$; open circles, values calculated by Ree and Hoover by integrating the pressure curve (see Ref. 3).

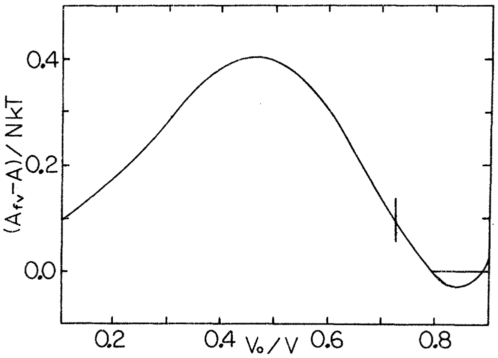

FIG. 3. Free energy per particle from Eq. (19) in the 16-particle free-volume limit A_{fv}/NkT minus that from the polynomial fit to the data in Eq. (26) A/NkT vs $\rho = V_0/V$. The vertical slash indicates the size of the standard deviation of the polynomial from the points to which it was fitted.

is actually due to the fact that the first two particles have much more freedom than the rest of the particles and weigh far more heavily in the 16-particle results than in the infinite limit. Beyond the phase-change region, this can be seen better, since there we can extrapolate Eqs. (19) and (20) to find the $N \to \infty$ limit. The only part of these equations which has been determined numerically is the constant. Solving Eq. (20) for $C_\infty = -\ln c_2$ gives

$$C_\infty = \frac{C_N + (\ln c_1)/N - [\ln(N-1)]/N}{1 - 2/N} \quad . \tag{27}$$

The constant c_1 can be estimated by simply drawing the rings for a 16-particle system into which the second particle could go. Assuming a width for each ring of $2b$ gives an area for the second particle of $10.4db$ or a determination that $c_1 = 10.4$, so that

$$C_\infty = -1.49 = -\ln[2\sqrt{3}(1.13)^2] \,, \tag{28}$$

where the 1.13 times b gives the effective distance between particle edges, such that the area of the hexagonal regions formed by the particles surrounding the site for a given particle with each on its equidistant mesh point represents the free volume into which the particle can be placed. The fact that the effective b is larger than the simple one can be interpreted as owing to the collective motions of the particles giving rise to larger areas for each particle than would be present if each moved independently. The 16-particle result here then would be expected to still give a free energy a bit too high, since only those collective motions involving 16 or fewer particles are possible. Taking the $N \to \infty$ limit in the crystal region anyway gives

$$[A(\rho) - A_i(\rho)]/NkT = -2\ln(\rho^{-1/2} - 1) - \ln\rho - 0.49,$$
$$0.79 \le \rho \le 1.0, \quad 2\sigma \approx 0.04 \tag{29}$$

where the increased accuracy estimate is due to the close agreement of the fit with the $\rho = 0.8858$ results which determine the constant C_{16}. At $\rho = 0.8$ where Ree and Hoover have also determined a beyond the phase-change value this gives $(A - A_i)/NkT = 4.01 \pm 0.04$ (two standard deviations) which as expected is a bit high compared to Ree and Hoover's 3.96 ± 0.01, probably owing to the truncation of collective motions as mentioned above.[3]

The pressure is related to A/NkT by

$$P = -\frac{\partial A}{\partial V} = \left(\frac{NV_p}{V}\right)^2 \frac{NkT}{NV_p} \frac{\partial(A/NkT)}{\partial(NV_p/V)} \,, \tag{30}$$

which with $V_0 = NV_p$ and $\rho = NV_p/V$ gives

$$\frac{PV_0}{NkT} = \frac{\rho^2\, \partial(A/NkT)}{\partial\rho} \quad . \tag{31}$$

The free energy per particle A/NkT was taken from Eq. (26) for $\rho \le 0.79$ and from the free-volume limit [Eq. (19)] for $\rho \ge 0.79$. The pressure was calculated, and the result is shown as a function of $\rho^{-1} = V/V_0$ in Fig. 4 along with the free-volume curve for lower densities and Ree and Hoover's Padé approximant to the $N \to \infty$ gas-region data.[5] The tie line gives a pressure for the phase change in the 16-particle system of $PV_0/NkT = 6.9$ which extrapolates to 7.6 when multiplied by the factor $\frac{32}{29}$ which can be deduced from Eq. (19). This is close to Alder and Wainwright's 870-particle result of 7.72. However, the phase-change region

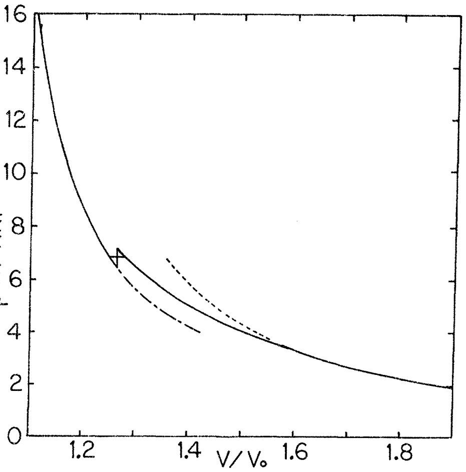

FIG. 4. Pressure vs $\rho^{-1} = V/V_0$. Dot-dashed line, P calculated from Eq. (19), the 16-particle free-volume limit; dashed line, the Padé approximant to the infinite-particle gas region (see Ref. 5); solid line, P calculated from Eq. (19) for $\rho \ge 0.79$ and from Eq. (26), the polynomial fit for $\rho \le 0.79$.

$1.25 \le V/V_0 \le 1.28$ is only about 0.6 of the $1.266 \le V/V_0 \le 1.312$ given by them.[1] This may be just $1/N$; however, a glance at Fig. 3 will show that the polynomial had trouble trying to equal zero for $\rho \ge 0.79$ and that if it had been forced to do so it would have had to be less steep for densities, just a bit less than 0.79, and steeper for densities a bit less. This is in the direction of correcting the disagreement so that it is a bit premature to blame it all on $1/N$ effects. One could conceivably play with fitting polynomials over smaller regions than that from 0 to 0.9, but the tendency to play with the regions chosen would be great, and the deviations of the polynomial when compared with the accuracy of the points really do not warrant this even though the resulting smoothing of the polynomial is probably largely responsible for the shrinking of the phase-change region.

To summarize the results, it has been found possible to evaluate the partition function for all densities. It was found that a system of only 16 particles with periodic boundaries could give enough information to find a good estimate for A/NkT in the crystal region for an infinite system. In addition a phase change can be seen in the 16-particle system from which the pressure at the phase change in an infinite system can be deduced in fair agreement with that found in an 870-particle system. In addition, of course, to the physics concerning nonoverlapping particles, etc., the fact that for $\rho \le 0.79$ the n_I's other than $I = 0$ in Eq. (11) suddenly became important, while they were not important before, provides a rather fascinating picture of gas states suddenly outnumbering crystal states for $\rho \le 0.79$. This possibly warrants further investigation.

VIII. OBSERVATIONS ABOUT THE METHOD

The biased selection method should be at its best in evaluating integrals of differences as indicated in Eq. (2), which has not been exploited at all here. The method also has some conceptual and practical advantages in regard to evaluating quantum-mechanical averages involving Jastrow wave functions, which are frequently done by solving an equivalent classical problem, in that it enables one to evaluate the integral directly. Finally this method, by avoiding the possibility of metastable states, enables one to use much smaller systems than is normally possible.

There are still a few drawbacks: The most serious problem is that of the trapezoidal rule which may simply be due to the nature of hard disks. For a softer potential the error term would be expected to be of the order of $1/d^2$ rather than $1/d$ as in this case. Another problem is that at present most of the computer time is spent removing points one at a time from the set of possible choices or worse yet checking to see if the points have already been removed. There are glimmerings of better ways in the author's mind, and while it would probably take a fair number of hours to find A/NkT for the eight or ten values of density and several values of d and N needed for each density to find out about the properties of the phase-change region rather than to just locate it, the better methods should reduce the time requirement by a factor of 10 and more likely by 20, thereby enabling us to see clearly and distinctly whether or not there is a van der Waals loop and to see what such things as the order parameter do in the phase-change region. This, in addition to work on liquid crystals and helium monolayers using generalizations of the techniques presented here, is currently under way.

ACKNOWLEDGMENTS

I wish to thank Washington and Lee University and especially O. Lee Dudley, the manager of data processing, for what must have seemed to be almost continuous use of its IBM 1130 computer during the developmental stages of this project. I would also like to acknowledge the aid of the Washington and Lee physics staff including George Gilmer who inspired the project; Edward F. Turner and George Mandeville who participated with me in seemingly endless discussion about averages of various quantities needed here; and Coleman Blake, a student at Washington and Lee during this time, who was involved in the project from its beginning and did much of the computer dirty work in addition to being involved in most of the discussion. Finally, I want to also thank Northwestern University for generously providing the computer time to finish this project which was started elsewhere.

APPENDIX

A system complicated enough to illustrate the biased selection method, yet still simple enough to follow in detail is the ring of nine lattice sites and four particles, each of which makes three sites unoccupiable, which is illustrated in Fig. 5. A diagram of the possible ways that the biased selection method might proceed after the first particle is placed on site 1 is also given. We note from the last line of the diagram that there are 24 ways in which one could get four particles in the system with the first one always going on site 1. Since the system is exactly the same with the first particle going on any other site, we can see that there must be $n_p N! = 216$ ways of putting the four particles into the system. In an honest Monte Carlo method where each new position is picked independently of the last choice there would be a probability of $216/9^4 = 8/243$ of finding the four particles

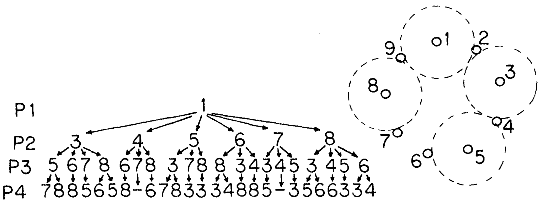

FIG. 5. Volume of nine lattice sites filled with four particles, along with a diagram of possible biased selection routes, after particle 1 has been placed on site 1.

to be nonoverlapping. In the biased selection method there is an equal chance of choosing only from the E_i occupiable sites available before the ith choice. We see from Fig. 5 then that E_1 is always 9 and E_2 is always 6 and that $E_3 = 4$ and $E_4 = 2$ for $\frac{2}{6} \times \frac{1}{2}$; $E_3 = 4$ and $E_4 = 1$ for $\frac{2}{6} \times \frac{1}{2}$; $E_3 = 3$ and $E_4 = 2$ for $\frac{2}{6} \times \frac{1}{3}$; $E_3 = 3$ and $E_4 = 1$ for $\frac{4}{6} \times \frac{2}{3}$; and finally $E_3 = 3$ and $E_4 = 0$ for $\frac{2}{6} \times \frac{1}{3}$ of the choices. If 36 choices are then assumed to have been made with exactly the statistically expected results, Eq. (7) gives

$$\begin{aligned} n_p N! &= \tfrac{1}{36}\, 9 \times 6\, [(4 \times 2)6 + (4 \times 1)6 + (3 \times 2)4 + (3 \times 1)16] \\ &= 216 \end{aligned}$$

just as it should. Furthermore nonzero estimates of this quantity occur for $\frac{8}{9}$ of the trials rather than for $\frac{8}{243}$ of the trials as in the honest method. The results of a single nonzero trial, however, vary from an estimate of $n_p N! = 9 \times 6 \times 4 \times 2 = 432$ to $n_p N! = 9 \times 6 \times 3 \times 1 = 162$, a sufficiently wide range to consider the possibility of averaging over the permutations of a given set.

Although there are nine different sets of q's which can be chosen, it can be seen from Fig. 5 that they must all be equivalent to rotations about the ring of the set (1, 3, 5, 8). Suppose that this set has been found and that it has been established that the probability of finding such a set in a given trial is the $\frac{8}{9}$ established above. Then noting that the various permutations with 1 first must give results identical to equivalent ones with 3 first, and that those with 5 first must give results identical to those with 8 first, and that these in turn must be identical to the permutations of the set (1, 3, 5, 7) with 1 first, Fig. 5 can be used to find that out of the 24 possible permutations of the set found there are eight with $E_3 = 4$ and $E_4 = 2$, four with $E_3 = 4$ and $E_4 = 1$, four with $E_3 = 3$ and $E_4 = 2$, and eight with $E_3 = 3$ and $E_4 = 1$. Thus $\bar{w}$ is given by

$$\begin{aligned} \bar{w} &= [1/(6 \times 9 \times 24)]\left(\tfrac{8}{8} + \tfrac{4}{4} + \tfrac{4}{6} + \tfrac{8}{3}\right) \\ &= 16/(3 \times 24 \times 6 \times 9), \end{aligned}$$

and Eq. (9) yields

$$n_p N! = \tfrac{8}{9}(3 \times 24 \times 6 \times 9)/16 = 216 \ .$$

Assuming that all permutations have entered as they statistically should, all of the error winds up in the determination of the $\frac{8}{9}$ probability of finding the set on a given trial.

Of course it will not be possible to average over an infinite number of permutations. However, the fact that Eqs. (7) and (9) are almost the same makes one suspect that indeed in the limit of a large number of trials $n_p N!$ can be accurately calculated no matter how many permutations are averaged over. This is easiest to see in the case of an artificial set which we will assume can appear in only one of two orders which are also the only two possible permutations of the set. One order gives rise to w_1 as its probability of being chosen and the other to w_2 as its probability. After a large number of trials Eq. (7) would yield

$$n_p N! = w_1(1/w_1) + w_2(1/w_2) = 2 \ .$$

Now suppose that after each choice the set is permuted once and the resulting w averaged with the original:

$$\begin{aligned} w_1 &\rightarrow \tfrac{1}{2}(w_1 + w_2) && \text{half of the time} \\ &\rightarrow \tfrac{1}{2}(w_1 + w_1) = w_1 && \text{half of the time} \end{aligned}$$

and

$$\begin{aligned} w_2 &\rightarrow \tfrac{1}{2}(w_2 + w_1) && \text{half of the time} \\ &\rightarrow w_2 && \text{half of the time} \end{aligned}$$

so that Eq. (9) will now yield

$$\begin{aligned} n_p N! &= \frac{\frac{1}{2} w_1 \times 2}{w_1 + w_2} + \frac{1}{2} + \frac{1}{2} w_2 \times \frac{2}{w_2 + w_1} + \frac{1}{2} \\ &= \frac{w_1 + w_2}{w_1 + w_2} + 1 = 2 \end{aligned}$$

as it should. The necessary trick is that the probability calculated from the order in which the set was actually discovered must be included in the average over permutations.

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Depolarization of Light in Atomic Fluids

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The experimental value of the polarizability anisotropy of a fluid is found to be an increasingly smaller fraction of the computer-calculated dipole-induced dipole anisotropy as the density is increased. This leads to the conclusion that the distortion of the polarizability of an individual atom from spherical symmetry produces an anisotropy which opposes and finally dominates the dipolar density anisotropy in determining the intensity of the depolarized light scattering.

During the past few years, a number of measurements of depolarized light scattering have been made on rare gases[1] and other nearly spherical molecules.[2] The reason why the measurements show a light scattering intensity at higher density, which is an order of magnitude less than that expected by extrapolation of the gas-phase results, remains unresolved.[3] In general, the scattering in a system of spherical atoms is due to dipoles produced by a fluctuating anisotropic field. The primary cause of such a field is a temporary asymmetric configuration of the atoms. Such an asymmetric density fluctuation can, however, also distort the electron density distribution of an atom so as to produce a polarizability of that atom which departs from spherical symmetry. In this electron-density-distortion contribution we include all the contributions to the macroscopic polarizability anisotropy due to causes other than the dipole-induced dipole mechanism. At low density, since the field a given atom experiences is that produced by interaction with only one other atom, the light scattering per atom varies linearly with density. At high density, since the neighboring atoms are more spherically distributed, the asymmetry is smaller, and one expects a decrease in the light-scattering intensity. The question of whether asymmetric density fluctuations lead predominantly to just a fluctuating dipole-induced dipole anisotropy or whether they lead predominantly to an anisotropy due to polarizability distortions is important to resolve. The calculation of the density fluctuations is a purely statistical-mechanical problem that can be considered exactly, and comparison with experiment can then establish the relative importance of the polarizability distortion which is difficult to estimate theoretically.

The statistical-mechanical calculations are difficult to perform rigorously at fluid densities without resort to computers since they involve fourth-order distribution functions. They have been carried out here primarily for hard spheres in the spirit of the van der Waals theory which assigns the attractive forces of real molecules a minor role. However, to check this point, a few systems consisting of atoms with square-well and Lennard-Jones interaction potentials have been studied as well.

The dipolar density fluctuation, which leads to light scattering is characterized by the second-rank tensor

$$T_{ij}^{XY} = \frac{1}{r_{ij}^3}\left(\delta_{XY} - \frac{3X_{ij}Y_{ij}}{r_{ij}^2}\right) , \tag{1}$$

where $X, Y = x, y, z$. In this formula, the capital-letter indices label the coordinates and the lower-case indices the atoms. The distance between atoms i and j is r_{ij}, and δ is the Kronecker δ. The light scattering per atom, if there is no electronic distortion, is proportional to the dimensionless quantity

$$S^{XY} = \frac{\sigma^6}{N}\left\langle\left(\sum_{i\neq j}^{N} T_{ij}^{XY}\right)^2\right\rangle , \tag{2}$$

that is, the statistical average of the square of the value of one of the tensor elements for a system of N spheres of diameter σ. This expression is valid in the long-wavelength limit, in which retardation effects are neglected. The tensor $\overleftrightarrow{T}$ also enters the theoretical expressions for a number of other phenomena such as the dielectric polarization of a nonpolar fluid[4] and the nuclear magnetic relaxation[5]