Studies in Molecular Dynamics. IV. The Pressure, Collision Rate, and Their Number Dependence for Hard Disks*

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The pressure for four, 12, and 72 hard disks determined dynamically from the virial theorem or the collision rate is shown to be identical to that determined by the Monte Carlo method. To show this equivalence, it is necessary to take into account that the center-of-mass velocity is kept fixed in the dynamic system. This numerical agreement suggests the validity of the quasiequidynamical hypothesis even for small systems. The \( \frac{\text{inN}/N}{\text{inN}} \) dependence of the phase-transition pressure on the number of particles \( N \) is simply explained in terms of the communal entropy.

I. INTRODUCTION

The equation of state for a small number of disks was originally investigated to determine whether or not the two-dimensional system would show a phase transition more convincingly than the three-dimensional hard-sphere system. For spheres the phase transition was not firmly established because the two phases only coexisted for the brief time of a rarely observed jump between the solid and liquid phases. The possibility of coexisting phases typical of a first-order phase transition was thought more likely in two-dimensional systems because boundary effects, which could inhibit coexistence, are less serious in two than in three dimensions for a given number of particles.

First, it was determined that disks behaved similarly to spheres in the phase-transition region for small numbers of particles; that is, for very small systems no phase transition is seen, while for slightly larger systems jumps between the two phases are observed, but coexistence is not achieved. Subsequently, a large system of 870 disks was investigated and showed the hoped-for coexisting phases. The behavior of 870 particles in the coexistence region has already been described; a more complete equation of state for that system, emphasizing accurate solid-phase thermodynamic properties, will be published in a separate paper.

In this paper, the effort is concentrated upon the less accurate results obtained for small systems, with particular emphasis upon the intercomparison of various ways to calculate numerically a thermodynamic property for identical systems. The most difficult problem of extrapolating finite system results to infinite systems has been discussed already by a number of workers, and this report touches upon this aspect only by pointing out that the predominant number dependence in the phase-transition region can be simply explained on the basis of the communal entropy.

In the intercomparison of finite systems the large effect of the nature of the boundary on the results is not discussed either. In a future report it will be shown that periodic boundaries generally lead to a smaller dependence of the results on the number of particles than hard-wall boundaries. However, it was found that the qualitative features of the equation of state, including the behavior in the phase transition, are independent of the boundary conditions used.

The intercomparison of the pressure of identical small periodic systems, as obtained dynamically and by the Monte Carlo method, involves the assumption that time averages are equivalent to statistical space averages. Insofar as numerical agreement between the data is obtained, the quasiequidynamical hypothesis is justified for small systems. Before discussing these results, the pressure obtained dynamically both by the virial theorem and the collision rate is compared. This is done to straighten out a previously unexplained discrepancy. Finally, another number-dependent effect, not previously discussed, arising only in the phase-transition region, is described and compared to the numerical data.

II. INTERCOMPARISON OF PRESSURE

The pressure has been determined dynamically in two different ways. The direct way is a straightforward application of the virial theorem. The pressure can also be determined indirectly, but also exactly, from the measured collision rate. In comparing these pressures, it is necessary to consider in detail the effect of keeping the velocity of the center of mass zero. The result of this constraint is to introduce velocity “correlations”; that is, once the velocity of a particular particle is known, the remaining particles must on the average be moving in the opposite direction. This accentuated motion of particles toward one another increases both the frequency and momentum transfer of collisions, and thus the pressure. When these increases, here
calculated to be of order $1/N$, where $N$ is the number of particles, are taken into account, it is found that both ways of calculating the pressure dynamically agree qualitatively.

In comparing the dynamic pressure with that calculated by the Monte Carlo method,\textsuperscript{4} the velocity "correlations"\textsuperscript{9} must again be taken into account. Once this is done, the agreement of the pressures is within the accuracy of the results. In this comparison, the accuracy of the Monte Carlo results suffers somewhat inasmuch as an extrapolation of the pair distribution to its value at contact is required, while no such extrapolation is required dynamically. It is also interesting to point out that the fluctuations in pressure are not the same in the three different methods of calculating the pressure. The pressure calculated by the virial theorem converges more rapidly to its equilibrium value than the one calculated by the collision rate. The pressures obtained by the Monte Carlo method and collision rate are roughly comparable in their convergence rates.

The dynamic pressure calculation is based on the virial theorem,

$$\frac{\langle PA/NT \rangle - 1}{\langle \langle PA/NT \rangle \rangle} = \left[ \sum_{i=1}^{N} \frac{r_i v_i}{m} \right]^2 = \left[ N \langle u \rangle \right]^2,$$

where the final sum is over all collisions $c$, occurring in the time $\tau$. The compressibility factor, $\langle PA/NT \rangle$, is given in terms of the particle mass $m$ and the particles' coordinates, velocities, and forces, $r_i$, $v_i$, $F_i$ respectively. The mean-squared velocity is $\langle u \rangle^2$ and the brackets $\langle \langle \rangle \rangle$ indicate an average over the time $\tau$, which has to be sufficiently long. In the last part of Eq. (1), the time average is replaced by a collision average of the velocity changes upon collision. Since these velocity changes upon collision are independent of density for hard particles (only binary collisions), these can be readily calculated. The sum over collisions, divided by $\tau$, can thus be written as a product of the average velocity change per collision times the density-dependent collision rate. One can now proceed by either evaluating the velocity change per collision or alternatively by taking the ratio of Eq. (1) with its low-density form:

$$\frac{\langle PA/NT \rangle - 1}{\langle \langle PA/NT \rangle \rangle} = \frac{\Gamma}{\Gamma_0},$$

where $\Gamma$ is the second virial coefficient, and $\Gamma_0$ is the ratio of the high-density to the low-density collision rate. Since the constraint of zero center-of-mass velocity is removed.

Table I. The dynamic equation of state for four hard disks with periodic boundary conditions.

<table>
<thead>
<tr>
<th>$A/A_0$</th>
<th>$PA/NT$*</th>
<th>1000 collisions</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.25</td>
<td>10.24</td>
<td>1</td>
</tr>
<tr>
<td>1.35</td>
<td>6.57</td>
<td>5</td>
</tr>
<tr>
<td>1.40</td>
<td>5.63</td>
<td>5</td>
</tr>
<tr>
<td>1.45</td>
<td>3.80</td>
<td>7</td>
</tr>
<tr>
<td>1.50</td>
<td>5.80</td>
<td>7</td>
</tr>
<tr>
<td>1.60</td>
<td>4.86</td>
<td>7</td>
</tr>
<tr>
<td>1.70</td>
<td>4.21</td>
<td>5</td>
</tr>
<tr>
<td>1.80</td>
<td>3.80</td>
<td>3</td>
</tr>
<tr>
<td>1.90</td>
<td>3.49</td>
<td>3</td>
</tr>
<tr>
<td>2.00</td>
<td>3.25</td>
<td>3</td>
</tr>
<tr>
<td>2.10</td>
<td>3.11</td>
<td>3</td>
</tr>
<tr>
<td>3.00</td>
<td>2.16</td>
<td>1</td>
</tr>
</tbody>
</table>

* These data are accurate within about 1%.

Table II. The equation of state for 12 hard disks with periodic boundary conditions. Comparison of dynamic and Monte Carlo results.

<table>
<thead>
<tr>
<th>$A/A_0$</th>
<th>$PA/NT$*</th>
<th>Monte Carlo</th>
<th>Adjusted Monte Carlo</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.100</td>
<td>21.9</td>
<td>20.62±0.09</td>
<td>22.40</td>
</tr>
<tr>
<td>1.250</td>
<td>9.99</td>
<td>9.18±0.06</td>
<td>9.93</td>
</tr>
<tr>
<td>1.350</td>
<td>8.10</td>
<td>7.42±0.08</td>
<td>8.01</td>
</tr>
<tr>
<td>1.400</td>
<td>7.42</td>
<td>6.86±0.08</td>
<td>7.39</td>
</tr>
<tr>
<td>1.450</td>
<td>6.86</td>
<td>6.27±0.09</td>
<td>6.75</td>
</tr>
<tr>
<td>1.500</td>
<td>6.61</td>
<td>6.23±0.08</td>
<td>6.99</td>
</tr>
<tr>
<td>1.550</td>
<td>6.33</td>
<td>5.91±0.05</td>
<td>6.36</td>
</tr>
<tr>
<td>1.600</td>
<td>6.17</td>
<td>5.79±0.06</td>
<td>6.22</td>
</tr>
<tr>
<td>1.650</td>
<td>5.94</td>
<td>5.52±0.06</td>
<td>5.94</td>
</tr>
<tr>
<td>1.700</td>
<td>5.56</td>
<td>5.23±0.07</td>
<td>5.61</td>
</tr>
<tr>
<td>1.750</td>
<td>5.20</td>
<td>4.99±0.07</td>
<td>4.99</td>
</tr>
<tr>
<td>1.800</td>
<td>4.50</td>
<td>4.07±0.06</td>
<td>4.34</td>
</tr>
<tr>
<td>1.850</td>
<td>3.93</td>
<td>3.37±0.06</td>
<td>3.59</td>
</tr>
<tr>
<td>1.900</td>
<td>3.54</td>
<td>3.37±0.06</td>
<td>3.59</td>
</tr>
<tr>
<td>1.950</td>
<td>3.30</td>
<td>3.37±0.06</td>
<td>3.59</td>
</tr>
<tr>
<td>2.000</td>
<td>3.10</td>
<td>3.37±0.06</td>
<td>3.59</td>
</tr>
</tbody>
</table>

These data are accurate within about 1%.
fixed center-of-mass system, have been obtained:

\[ B_2(N) = B_2(\infty) , \]
\[ B_3(N) = B_3(\infty) \left[ 1 + \left( \frac{0.557}{N} \right) \right] , \]
\[ B_4(N) = B_4(\infty) \left[ 1 + \left( \frac{0.708}{N} \right) \right] , \]
\[ B_5(N) = B_5(\infty) \left[ 1 + \left( \frac{0.74}{N} \right) \right] . \]

In conformity with these results, it is found that at low densities the pressure decreases from a 48- to a 72- to an 870-particle system, and that the latter is slightly higher than the pressure predicted on the basis of the virial coefficients for an infinite system. For smaller systems as well as at higher densities for the larger systems, the number dependence is found to be more complicated. This is because an additional number dependence arises in the higher virial coefficients which is connected with the interactions of chains of particles stretching completely across the system. This effect is difficult to account for. It is hence necessary to rely on the empirical observation that once systems larger than a few hundred particles are studied, the observed dependence of the results on the number of particles outside the two-phase region is smaller than the present statistical accuracy of the data. The number dependences in the pure phases thus become apparently rapidly negligible as the system increases in size.

In the phase-transition region there is an additional strong number dependence of the results. This is such that for the very small systems of 4 and 12 disks no signs of the first-order transition are evident. However, for two particles with periodic boundary conditions, a distorted van der Waals-like loop can be established at about the density and pressure where the larger systems have a first-order transition. This transition,

\[ \begin{align*}
A/N & = 2.00 \quad 3.39 \quad 3.00 \\
PA/NkT & = 1.28 \quad 3.84 \quad 3.00 \\
1000 & \text{collisions} \\
1.31 & \quad 9.20 \pm 0.07 \\
1.80 & \quad -1.24 \\
1.90 & \quad 3.78 \\
1.70 & \quad -1.64 \\
1.55 & \quad 6.08 \\
1.50 & \quad 6.67 \\
1.45 & \quad 7.47 \\
1.40 & \quad 8.25 \\
1.36 & \quad 9.20 \pm 0.07 \\
1.34 & \quad 9.44 \pm 0.3 \\
1.32 & \quad 9.80 \pm 0.3 \\
1.31 & \quad 9.20 \pm 0.07 \\
1.28 & \quad 9.28 \pm 0.01 \\
1.25 & \quad 10.06 \\
1.20 & \quad 10.89 \\
1.15 & \quad 11.70 \\
1.10 & \quad 12.06 \\
1.05 & \quad 12.60 \\
1.00 & \quad 13.00 \\
0.95 & \quad 13.25 \\
0.90 & \quad 13.70 \\
0.85 & \quad 14.10 \\
0.80 & \quad 15.50 \\
0.75 & \quad 16.50 \\
0.70 & \quad 17.50 \\
0.65 & \quad 19.00 \\
0.60 & \quad 20.00 \\
0.55 & \quad 20.75 \\
0.50 & \quad 21.25 \\
0.45 & \quad 22.00 \\
0.40 & \quad 22.75 \\
0.35 & \quad 23.50 \\
0.30 & \quad 24.00 \\
0.25 & \quad 25.00 \\
0.20 & \quad 27.00 \\
0.15 & \quad 30.00 \\
0.10 & \quad 30.00 \\
0.05 & \quad 30.00 \\
0.00 & \quad 30.00
\end{align*} \]

for two particles of melti- of high dependence.

The expressions given in Ref. 5, using the exact infinite-system virial coefficients through \( B_4 \) [J. S. Rowlinson, Mol. Phys. 7, 593 (1963)]; \( B_6 \) [H. Ree and W. G. Hoover, ibid. 40, 939 (1964)] and the Monte Carlo estimate for \( B_4 \) [F. H. Ree and W. G. Hoover, ibid. 40, 939 (1964)], were multiplied by \( \left[ 1 + \left( \frac{1}{N} \right) \right] \) to get these results.

\[ 7 \quad \text{B. J. Alder, W. G. Hoover, and T. E. Wainwright, Phys. Rev. Letters 11, 241 (1963).} \]

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\[ \sigma \] The pressure calculated in this way is not equivalent to that obtained dynamically unless account is taken of the difference in the center-of-mass motion. As above, the fixed center of mass leads to a larger pressure by the dynamic method as given by the relation,

\[ \left( \frac{PA}{NkT} \right)_{\text{dynam}} = \frac{N}{N-1} \left( \frac{PA}{NkT} \right)_{\text{Monte Carlo}} \]

Once this adjustment is made the two alternative schemes yield, within the accuracy of the numerical data, identical results, as shown in Table II. This self-consistency of the numerical work then gives evidence for the assumption of quasirandomicity for finite systems.

III. COMMUNAL ENTROPY

The question of how to deduce rigorously from these computer studies of finite systems the behavior of infinite systems presents formidable problems. It is necessary theoretically to predict the dependence of the results on the number of particles so as to be able to extrapolate. This is, in general, a more difficult problem than to solve the infinite case in the first place. Part of the difficulty is that a number of different effects have to be considered and that these in turn depend on the nature of the boundary conditions.

One of the finite-number effects that can be rigorously corrected for with periodic boundary conditions is the usual neglect of a small integer compared to the number of particles \( N \); that is, \( N-1 \) can no longer be replaced by \( N \). This leads to a correction\(^8\) to the \( n \)th virial coefficient \( B_n \), whose leading term is of order \( 1/N \). The results, to order \( 1/N \), for the first few virial coefficients for disks, when these are calculated in a
for two particles, which is believed to be a crude model of melting, is to be contrasted with the fake transitions of higher order present in all small systems when the
analytic form of the partition function changes. Examples of these fake transitions are given in Appendix B, where the behavior of four hard squares is evaluated for both rigid and periodic boundary conditions. This example also illustrates that the nature of the boundary conditions in small systems can effect the phase transition qualitatively. Both four-particle systems have two phase transitions, but all are of higher order except that again in the periodic case one is first order. For the larger system of 870 disks, however, as pointed out before, the same behavior in the phase-transition region was established with either rigid or periodic boundary conditions.

The absence of a first-order phase transition for small systems (4 and 12), the lack of coexistence for slightly larger systems (48), and the van der Waals-like loop for still larger systems (72 and 870) can all be qualitatively explained on the basis of interfacial tension.\(^7\)\(^8\) The interfacial free energy in small systems is so large, even if the surface is kept to a minimum size, that coexistence is energetically prevented. The van der Waals-like loop arises from stabilization of the predominant phase by the surface terms. A quantitative analysis of the 870-particle results reveals, however, a shortcoming of this argument, in that the surface free energy per particle is rather small, \(kT/60\).

Besides the qualitative differences in the phase transition for small numbers of particles, it is desirable to establish, once the two phases coexist, how the phase-transition shifts with still further increase in size of the system. The important thing in extrapolating to infinite systems is to make sure that the phase transition does not change in character again, or disappear entirely for macroscopic systems. It is thus gratifying to be able to calculate quantitatively the difference between the transition pressures for 72 and 870 particles. Although in the 72-particle system the pressure fluctuations are large since the two phases just begin to coexist, the tie line connecting the fluid and solid isotherms can be quite well determined without going to the large computational effort\(^8\) required to establish the van der Waals-like loop accurately.

The predominating dependence of the transition pressure on the size of the system once the phases can coexist can be simply traced to the number dependence of the communal entropy. The entropy change across the transition \(\Delta S\) is related to the transition pressure for hard-particle systems by the thermodynamic requirement of equal chemical potentials in the two phases,

\[
P(N) \frac{\Delta A}{NkT} = \frac{\Delta S(N)}{Nk},
\]

where \(\Delta A\) is the area change across the transition.

The value of \(\Delta A\) has been established to be nearly the same for both the 72- and 870-particle systems, namely \(\Delta A/\Delta s = 0.05\), where \(\Delta s\) is the area at close packing. The transition pressure, on the other hand, was found to be more strongly dependent on the size of the system than the pressure in the one-phase regions and thus, similarly, must the transition entropy be strongly dependent on \(N\). Although the major contribution to the transition entropy does not arise from the communal entropy but rather from the area expansion,\(^2\) the major number dependence does arise from communal entropy since, as was just pointed out, the area expansion is only weakly dependent on \(N\).

The appearance of the communal entropy across the phase transition is justified here since for the larger systems under consideration both the solid and fluid phases exist. Both the free area per particle \(a_f\) to which a solid particle is confined and the volume accessible to a fluid particle \((A - Nb)\), the total area less the effective area of the particles, must be properly taken into account to calculate quantitatively the communal entropy.\(^9\) However, to calculate the number dependence of the communal entropy it suffices to make the usual qualitative arguments, namely that the configurational partition function of the solid, \((a_f)^N \sim (A/N)^N\), differs from that of the liquid, \((A - Nb)^N/N \sim A^N/N!\), by the indistinguishability of the particles. Under these simple approximations the transition entropy is, with the aid of Stirling's approximation for \(N!\),

\[
\Delta S(N)/Nk = \text{const} - \left[ \ln(2\pi N)^{1/2}/N \right] + O(N^{-2}),
\]

with the value of the constant of unity. A quantitative calculation leads to a value of the constant of 0.36, the communal entropy part of which is an order of magnitude smaller. From the number-dependent part of the communal entropy, \(-\frac{1}{2} \ln(2\pi N)/N\), the pressure shift of the tie line is calculated:

\[
[\Delta S(870)/Nk] - [\Delta S(72)/Nk] = -\frac{1}{144} \ln(1740\pi) + \frac{1}{144} \ln(144\pi) = 0.038,
\]

\[
[P(870) - P(72)] A_0 / NkT = 0.76,
\]

by using the previously determined area change. This calculated difference in the transition pressures corresponds closely to the one found numerically, as shown in Fig. 2. The communal entropy argument leads to a shift of \(PA_0/NkT\) from 7.7 at the 870-particle transition to 7.8 for the infinite system, provided it can still be assumed that the area change remains constant.

The same \((\ln N)/N\) dependence of the transition pressure should be found in three dimensions. Since hard-sphere systems large enough for the two phases to coexist have not been studied, the transition pressure

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\(^8\) Only for one-dimensional hard spheres has an exact calculation of the communal entropy been carried out [W. G. Hoover and B. J. Alder, J. Chem. Phys. 45, 2361 (1966)].
A/Ao --+

**Fig. 2.** Hard-disk equation of state. Dynamic results for 72 disks are indicated by bullets (0). The two smooth curves shown fit the high-density 870-particle isotherm and the low-density virial series. Both the 72 and 870 tie lines are shown. The vertical arrow indicates the magnitude of the difference in transition pressures between 72 and 870 as predicted from the N dependence of the communal entropy.

for each value of N can be roughly identified with the fluid pressure at the highest density for which the jump from solid to the fluid can be observed. The N dependence of this estimated transition pressure is found to be in agreement with the \((\ln N)/N\) prediction. It thus appears that even in the phase-transition region the pressure is within 0.1% of its infinite-system value so that, for practical purposes, the results are indistinguishable from those in the thermodynamic limit once N exceeds about 10,000.

**APPENDIX A**

The second virial coefficient and the low-density collision rate are calculated for D-dimensional hard particles. The system has periodic boundary conditions and zero center-of-mass velocity. The velocity "correlations" present because the center-of-mass velocity is zero tend to increase both the collision rate and the second virial coefficient for finite systems. The velocity space probability density, \(P_1(v)\), is assumed to be Maxwellian for a typical particle, (1) for example,

\[
P_1(v) = \left[ \frac{D}{(2\pi \sigma^2)^{D/2}} \right] \exp\left( -\frac{Dv^2}{2\sigma^2} \right),
\]

where \(D\) is the number of dimensions. The Maxwellian assumption is distorted at the high-velocity tail because the maximum speed is of order \(N^{1/2}u\); even for \(N\) as small as four, the approximation is adequate for present purposes.

The remaining momentum, \(N\vec{v} - \vec{v}_i = -\vec{v}_i\), and energy, \(N\sigma^2 - v_i^2\), is, on the average, distributed equally among the remaining \(N - 1\) particles. Any one of these particles, (2) for example, will also have a Maxwellian velocity distribution, but with most probable velocity \(-\vec{v}_i/(N - 1)\):

\[
P_2(v_i; v_0) = \left[ \frac{D}{2\pi \sigma^2} \right]^{D/2} \exp\left( -\frac{D(v_i + [v_i/(N - 1)]^2)}{2\sigma^2} \right),
\]

\[\xi^2 = \left[ \frac{(N\sigma^2 - v_i^2)}{(N - 1)} \right] - \left[ \frac{v_i^2}{(N - 1)} \right].\]

Effects of order \(1/N\) can be calculated by expanding \(P_2(v_i; v_0)\),

\[
P_2(v_i; v_0) = P_1(v_0) \left[ 1 + D\frac{v_i^2}{(N - 1)} - \frac{v_i^2}{2(N - 1)^2} \right]/(2N\sigma^4).
\]

Using the probability density (A4), the calculation of the low-density collision rate \(\Gamma_0\) and the average rate of momentum transfer \(\langle \sum \mathbf{F}_c \cdot \mathbf{r}_c \rangle_0\) can be carried out in the usual way:

\[
\Gamma_0 = \left[ \frac{2DB_2(N)}{\sigma V} \right] \int \int P(v_i)P(v_i; v_0)(\dot{x}_1 - \dot{x}_2)dv_i dv_0,
\]

\[\dot{x}_1 > \dot{x}_2\]

\[
= \frac{2DB_2(N)}{\sigma V(\dot{x}_1^2 + 1)} \left( 1 + \frac{4D + 1}{8ND} \right),\]

\[\langle \sum \mathbf{F}_c \cdot \mathbf{r}_c \rangle_0 = \left[ \frac{2DB_2(N)}{V} \right] \int \int \dot{x}_1 > \dot{x}_2
\[
\times P(v_i)P(v_i; v_0)(\dot{x}_1 - \dot{x}_2)dv_i dv_0
\]

\[= \left[ \frac{2B_2(N)}{V} \right] \left( 1 + \frac{N - 1}{1} \right).\]

In each equation the last factor in the parentheses is the deviation of the result from that obtained without the fixed center-of-mass restriction.

The collision rate is increased by about \(1 + (2N)^{-1}\), and the effective second virial coefficient by \(1 + (1/N)\). \(B_2\) is \(\sigma, \pi\sigma^2/2,\) and \(2\pi\sigma^2/3\) in one, two, and three dimensions, respectively. Thus the dynamic system, through the second virial coefficient, has the low-density equation-of-state characteristic of an infinite system, the velocity correlations just canceling out the usual \(N\) dependence (which comes from the binomial coefficient \(\binom{N}{2}\)).
The configurational integrals for four hard parallel squares of unit sidellength can be evaluated for both periodic and rigid-boundary conditions. These results show that (1) the free-volume form of the equation of state is obtained in the rigid-boundary case, and (2) a looped isotherm is found in the periodic case. The configurational integral is defined in the usual way:

\[ Q_i = (4!)^{-1} \int_A \exp\left(\frac{-\Phi}{kT}\right) d\mathbf{r}^i, \]

(B1)

where \( \Phi \) is the potential energy of the system. The region of integration is the square container of area \( A \).

The integral is most easily evaluated by expanding the exponential in Mayer \( f \) functions. The resulting integrals, which are related to simple one-dimensional integrals, can then be evaluated. The results are as follows:

\[ Q_4 \text{ (Periodic Boundary):} \]

\[ 4 < A < 9: \quad \frac{A}{4} (A^{1/2} + 1) (A^{1/2} - 2)^3, \]

\[ 9 < A < 16: \quad \frac{A}{4} \left(4A^4 - 24A^{7/2} + 168A^3 - 1312A^{5/2} + 4836A^2 - 7680A^{3/2} + 4280A\right), \]

(B2)

\[ 16 < A \]

\[ \frac{A}{4} \left(3A^4 - 72A^2 + 612A - 1864A\right). \]

\[ Q_4 \text{ (Rigid Boundary):} \]

\[ 4 < A < 9: \quad \frac{1}{2}\sqrt{A} (A^{1/2} - 2)^3, \]

\[ 9 < A < 16: \quad \frac{1}{2}\sqrt{A} \left(11A^4 - 64A^{7/2} - 400A^3 + 4736A^{5/2} - 16988A^2 + 26496A^{3/2} - 11296A - 13520A^{1/2} + 11426\right), \]

(B3)

\[ 16 < A \]

\[ \frac{1}{2}\sqrt{A} \left(12A^4 - 96A^{7/2} + 48A^3 + 1344A^{5/2} - 2544A^2 - 5952A^{3/2} + 15456A + 7984A^{1/2} - 26462\right). \]

The isotherms corresponding to the two kinds of boundary conditions are shown in Fig. 3. In plotting the periodic boundary case \( PA/NkT - 1 \) has been multiplied by \( \frac{1}{3} \), so that the results correspond to a system with a fixed center of mass.