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Many-Body Problem in Quantum Statistical Mechanics. I. General Formulation*

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A formulation is given whereby the grand partition function of a many-body system satisfying Bose-Einstein or Fermi-Dirac statistics is expressed in terms of certain U functions defined for the same system with Boltzmann statistics. It is then shown that these U functions can be evaluated in successive approximations in terms of a binary kernel B which can be computed from a solution of the two-body problem. The approach to the limit of infinite volume is studied. The example of a hard sphere interaction is discussed in some detail.

1. INTRODUCTION

THE present series of papers is devoted to a method of treating the many-body problem in quantum-statistical mechanics. Much of this work was performed in the summer and the fall of 1956 and has been reported[1] in abbreviated versions before.

From the general formulations of statistical mechanics it is known that the thermodynamical properties of a system can be obtained from its partition function. However, the actual task of evaluating the partition function from the atomic or molecular interactions is both complicated and difficult. In classical statistical mechanics, for a system in the gaseous phase, the problem has been reduced to a series of quadratures through the work of Mayer and others.[2] In quantum mechanics, the enormous difficulty of solving the N-body eigenvalue problem ($N\geq 3$), allows so far only for a systematic method[3] of computing the second virial coefficient, and for computations[4] of the quantum corrections to the classical results. For a discussion of phenomena at very low temperatures (e.g., the problem of Bose-Einstein transition and the problem of the many-body ground-state energy) where quantum effects are dominant, these known methods[5] are not applicable.

The purpose of this and the subsequent papers is to develop a systematic method that is suitable to treat problems in which quantum effects are important. The general procedure followed is to first separate out the effect of the statistics (i.e., Bose-Einstein statistics or Fermi-Dirac statistics) of the quantum-mechanical problem and to express the grand partition function in terms of certain U functions defined in terms of the quantum-mechanical problem with Boltzmann statistics. Such a separation of the effect of statistics is formulated in general in this paper and will be further developed in later papers. It is particularly useful in treating the phenomena of Bose-Einstein condensation.

The second step is to formulate a method whereby these U functions can be computed from a solution of the two-body problem. In effect, the computation of U is through an expansion, loosely speaking, in powers of a function, called the binary kernel, which is obtainable from a solution of the two-body problem. The method is applicable in cases where the two-body interaction may contain a singular repulsive core.

For the gaseous phase the formulation in this paper yields a recipe, much like Mayer's method in classical statistical mechanics, for computing the equation of state through a series of quadratures. The method can also be used to calculate the ground-state energy, to obtain the limiting forms of thermodynamical functions at very low temperatures and to study the problem of Bose-Einstein transition. These topics will be discussed in later papers.

2. SOME DEFINITIONS

We consider an N-particle Hamiltonian

$$H_N=-\sum_{i=1}^{N} \nabla_i^2+\sum_{i>j} V(\mathbf{r}_i-\mathbf{r}_j), \tag{I.1}$$

where for simplicity units are chosen so that $\hbar=1$ and mass of the particles $=\frac{1}{2}$. Three- and more-particle interactions are not considered, although their inclusion would not introduce real complications in much of the following discussions.

To be specific, the N particles are considered to move in a cubic box of dimensions $L\times L\times L$ with *periodic boundary conditions*. We use the symbol $\Omega=L^3$ for the volume of the box.

We now discuss separately the cases when the

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[1] International Conference on Theoretical Physics at Seattle, September, 1956 (unpublished); *Conference on the Many-Body Problem, Stevens Institute, Hoboken, New Jersey, January, 1957* (to be published). Some preliminary results have been summarized in T. D. Lee and C. N. Yang, Phys. Rev. **105**, 1119 (1957).

[2] H. D. Ursell, Proc. Cambridge Phil. Soc. **23**, 685 (1927). J. E. Mayer, J. Chem. Phys. **5**, 67 (1937); J. E. Mayer *et al.*, J. Chem. Phys. **5**, 74 (1937); **6**, 87 (1938); **6**, 101 (1938).

[3] G. E. Uhlenbeck and E. Beth, Physica **3**, 729 (1936); **4**, 915 (1937). For other references, see, e.g., D. ter Haar, *Elements of Statistical Mechanics* (Rinehart and Company, New York, 1954).

[4] See, e.g., J. de Boer's review article in *Reports on Progress in Physics* (The Physical Society, London, 1949), Vol. 12, p. 305, Sec. 6(III).

[5] See some recent developments: W. B. Riesenfeld and K. M. Watson, Phys. Rev. **104**, 492 (1956); **108**, 518 (1957); A. J. F. Siegert and Ei Teramoto, Phys. Rev. **110**, 1232 (1958); E. W. Montroll and J. C. Ward, Phys. Fluids **1**, 55 (1958).

particles satisfy Boltzmann, Bose-Einstein, and Fermi-Dirac statistics.

A. Boltzmann Statistics

We follow the standard treatment and introduce the operator

$$W_N \equiv \exp(-\beta H_N), \tag{I.2}$$

where

$$\beta = (\kappa T)^{-1}. \tag{I.3}$$

We shall also use the thermal wavelength

$$\lambda = (4\pi\beta)^{\frac{1}{2}}.$$

The matrix elements of W_N in coordinate representation is

$$\langle 1',2'\cdots N' | W_N | 1,2\cdots N\rangle = \sum_i \psi_i(1',2'\cdots N')\psi_i^*(1,2\cdots N) \exp(-\beta E_i). \tag{I.4}$$

Here

$$1 \equiv \mathbf{r}_1 \equiv (x_1,y_1,z_1), \text{ etc.,} \quad 1' \equiv \mathbf{r}_1' \equiv (x_1',y_1'z_1'), \text{ etc.,}$$

and $\psi_i(\mathbf{r}_\alpha)$, E_i are the normalized eigenfunctions and eigenvalues of H_N with *periodic boundary conditions* in a cubic box of volume Ω. The summation in (I.4) extends over all eigenfunctions ψ_i. It is useful to notice that the exchange of any pair $\mathbf{r}_i'$, $\mathbf{r}_i$ with $\mathbf{r}_j'$, $\mathbf{r}_j$ leaves W_N unchanged.

The partition function is

$$Q_0 \equiv 1,$$

$$Q_N \equiv \sum_i \exp(-\beta E_i) = \int_\Omega \langle 1,2\cdots N | W_N | 1,2\cdots N\rangle d^{3N}r. \tag{I.5}$$

To obtain the logarithm of the grand partition function in a simple form we follow a procedure first introduced by Ursell[2] and by Mayer[2] for classical statistical mechanics and by[6] Kahn and Uhlenbeck for quantum-statistical mechanics. One defines U_l functions by

$$\begin{aligned}
\langle 1' | W_1 | 1\rangle &\equiv \langle 1' | U_1 | 1\rangle, \\
\langle 1',2' | W_2 | 1,2\rangle &\equiv \langle 1' | U_1 | 1\rangle\langle 2' | U_1 | 2\rangle + \langle 1',2' | U_2 | 1,2\rangle, \\
\langle 1',2',3' | W_3 | 1,2,3\rangle &\equiv \langle 1' | U_1 | 1\rangle\langle 2' | U_1 | 2\rangle\langle 3' | U_1 | 3\rangle \\
&\quad + \langle 1' | U_1 | 1\rangle\langle 2',3' | U_2 | 2,3\rangle \\
&\quad + \langle 2' | U_1 | 2\rangle\langle 1',3' | U_2 | 1,3\rangle \\
&\quad + \langle 3' | U_1 | 3\rangle\langle 1',2' | U_2 | 1,2\rangle \\
&\quad + \langle 1',2'3' | U_3 | 1,2,3\rangle, \text{ etc.}
\end{aligned} \tag{I.6}$$

Putting $\mathbf{r}_1 = \mathbf{r}_1'$, $\mathbf{r}_2 = \mathbf{r}_2'$ in these equations and integrating over $\mathbf{r}_1$, $\mathbf{r}_2$, $\cdots$, one can show[2,6] that

$$\mathcal{Q}_\Omega \equiv \sum_{N=0}^{\infty} (N!)^{-1} Q_N z^N = \exp\left\{\sum_{l=1}^{\infty} z^l (l!)^{-1} \int_\Omega \langle 1,\cdots,l | U_l | 1,\cdots,l\rangle d^{3l}r\right\}. \tag{I.7}$$

For the sake of completeness we give a proof of this formula in Appendix A.

According to the principles of statistical mechanics, the equilibrium pressure p and density ρ of the system are given by

$$\frac{p}{\kappa T} = \lim_{\Omega\to\infty} \Omega^{-1} \ln \mathcal{Q}_\Omega,$$

and

$$\rho = \lim_{\Omega\to\infty} \Omega^{-1} (\partial \ln \mathcal{Q}_\Omega / \partial \ln z). \tag{I.8}$$

Using (I.7) one obtains

$$\frac{p}{\kappa T} = \lim_{\Omega\to\infty} \sum_{l=1}^{\infty} b_l(\Omega) z^l,$$

$$\rho = \lim_{\Omega\to\infty} \sum_{l=1}^{\infty} l b_l(\Omega) z^l, \tag{I.9}$$

where

$$b_l(\Omega) = (l!\Omega)^{-1} \int_\Omega \langle 1,\cdots,l | U_l | 1,\cdots,l\rangle d^{3l}r. \tag{I.10}$$

It is important to remember that the W and U functions are defined for fixed Ω. The question of whether $b_l(\Omega)$ approaches a limit as $\Omega \to \infty$ will be discussed in Sec. 5.

B. Bose-Einstein (i.e., Symmetrical) Statistics

For symmetrical statistics, the corresponding function $W_N{}^S$ is

$$\langle 1',2',\cdots,N' | W_N{}^S | 1,2,\cdots,N\rangle \equiv N! \sum_{\text{sym. } \psi} \psi_i(1',2',\cdots,N') \times \psi_i^*(1,2,\cdots,N) \exp(-\beta E_i). \tag{I.11}$$

We define

$$Q_0{}^S \equiv 1, \quad Q_N{}^S \equiv \int_\Omega \langle 1,2,\cdots,N | W_N{}^S | 1,2,\cdots,N\rangle d^{3N}r.$$

We also define $U_l{}^S$ functions in complete analogy with (I.6):

$$\begin{aligned}
\langle 1' | W_1{}^S | 1\rangle &\equiv \langle 1' | U_1{}^S | 1\rangle, \\
\langle 1',2' | W_2{}^S | 1,2\rangle &\equiv \langle 1' | U_1{}^S | 1\rangle\langle 2' | U_1{}^S | 2\rangle + \langle 1',2' | U_2{}^S | 1,2\rangle, \text{ etc.}
\end{aligned} \tag{I.12}$$

[6] B. Kahn and G. E. Uhlenbeck, Physica 5, 399 (1938).

The grand partition function is

$$\mathcal{Q}_\Omega^S \equiv \sum (N!)^{-1} Q_N^S z^N = \exp\left\{ \sum_{l=1}^{\infty} (l!)^{-1} z^l \int_\Omega \langle 1,\cdots,l | U_l^S | 1,\cdots,l \rangle d^{3l}r \right\}, \quad \text{(I.13)}$$

which is proved in the same way that (I.7) was proved. One obtains then again (I.9) with b_l replaced by b_l^S, where

$$b_l^S(\Omega) = (l!\Omega)^{-1} \int \langle 1,\cdots,l | U_l^S | 1,\cdots,l \rangle d^{3l}r. \quad \text{(I.14)}$$

C. Fermi-Dirac (i.e., Antisymmetrical) Statistics

For antisymmetrical statistics one has

$$\langle 1',2',\cdots,N' | W_N^A | 1,2,\cdots,N \rangle = \sum_{\text{antisym. } \psi} \psi_i(1',2',\cdots,N') \times \psi_i^*(1,2,\cdots,N) \exp(-\beta E_i). \quad \text{(I.15)}$$

Equations (I.12), (I.13), and (I.14) remain the same in form if one replaces all superscripts S (for symmetrical statistics) by A (for antisymmetrical statistics).

In the following we list some simple examples to illustrate these definitions:

Example 1:

$$\langle 1' | W_1 | 1 \rangle = \langle 1' | W_1^S | 1 \rangle = \langle 1' | W_1^A | 1 \rangle = \langle 1' | U_1 | 1 \rangle = \sum_{\mathbf{k}} \Omega^{-1} \exp[i\mathbf{k}\cdot(\mathbf{r}_1 - \mathbf{r}_1') - \beta \mathbf{k}^2], \quad \text{(I.16)}$$

where the summation extends over $\mathbf{k} = 2\pi L^{-1}(l,m,n)$ with l, m, $n = 0$ and $\pm$ integers. In the limit $\Omega \rightarrow \infty$,

$$\langle 1' | U_1 | 1 \rangle \rightarrow (8\pi^3)^{-1} \int d^3k \exp[i\mathbf{k}\cdot(\mathbf{r}_1 - \mathbf{r}_1') - \beta \mathbf{k}^2] = \lambda^{-3} \exp[-(\mathbf{r}_1 - \mathbf{r}_1')^2/(4\beta)]. \quad \text{(I.17)}$$

One easily computes b_1:

$$b_1(\Omega) = b_1^S(\Omega) = b_1^A(\Omega) = \sum_{\mathbf{k}} \Omega^{-1} \exp(-\beta \mathbf{k}^2). \quad \text{(I.18)}$$

In the limit $\Omega \rightarrow \infty$, one obtains

$$b_1(\Omega) \rightarrow \lambda^{-3}. \quad \text{(I.19)}$$

Example 2:

For free particles it is clear from the definition (I.4) that

$$\langle 1',\cdots,N' | W_N | 1,\cdots,N \rangle = \langle 1' | W_1 | 1 \rangle \langle 2' | W_1 | 2 \rangle \cdots \langle N' | W_1 | N \rangle.$$

Hence one obtains from (I.6)

$$U_2 = 0, \quad U_3 = 0, \quad \text{etc.} \quad \text{(I.20)}$$

Example 3:

For Bose-Einstein statistics, the wave functions for two free particles are

$$\psi = \Omega^{-1} \exp[i\mathbf{k}\cdot\mathbf{r}_1 + i\mathbf{k}\cdot\mathbf{r}_2],$$

and

$$\psi = 2^{-\frac{1}{2}}\Omega^{-1}[\exp(i\mathbf{k}_a\cdot\mathbf{r}_1 + i\mathbf{k}_b\cdot\mathbf{r}_2) + \exp(i\mathbf{k}_b\cdot\mathbf{r}_1 + i\mathbf{k}_a\cdot\mathbf{r}_2)], \quad (\mathbf{k}_a \neq \mathbf{k}_b).$$

Substituting these into (I.11), one obtains

$$\langle 1',2' | W_2^S | 1,2 \rangle = \langle 1' | W_1 | 1 \rangle \langle 2' | W_1 | 2 \rangle + \langle 2' | W_1 | 1 \rangle \langle 1' | W_1 | 2 \rangle.$$

Comparison with (I.12) shows therefore that for free particles

$$\langle 1',2' | U_2^S | 1,2 \rangle = \langle 2' | W_1 | 1 \rangle \langle 1' | W_1 | 2 \rangle. \quad \text{(I.21)}$$

Similarly one finds

$$\langle 1',2' | U_2^A | 1,2 \rangle = -\langle 2' | W_1 | 1 \rangle \langle 1' | W_1 | 2 \rangle. \quad \text{(I.22)}$$

3. U_N^S AND U_N^A IN TERMS OF U_N

In the last section we wrote down the main formulas in the Ursell-Mayer-Kahn-Uhlenbeck treatment of the equations of state. To calculate the coefficients b_l, b_l^S, and b_l^A one first calculates the functions U_l, U_l^S, and U_l^A. Now the functions U_l^S and U_l^A are considerably more complicated than U_l. [We saw, e.g., in (I.20) and (I.21) that for free particles, U_2, $U_3 \cdots$ vanish, but not U_2^S and U_2^A.] In this section we shall formulate explicit rules by which U_N^S and U_N^A can be computed once the functions U_N are known.

Such rules exist because the U's are defined in terms of the W's, and the W's as defined in (I.4), (I.11), and (I.15) are related through the equations

$$\langle 1',\cdots,N' | W_N^S | 1,\cdots,N \rangle = \sum_{P'} P' \langle 1',\cdots,N' | W_N | 1,\cdots,N \rangle, \quad \text{(I.23)}$$

and

$$\langle 1',\cdots,N' | W_N^A | 1,\cdots,N \rangle = \sum_{P'} \mathcal{C}_{P'} P' \langle 1',\cdots,N' | W_N | 1,\cdots,N \rangle, \quad \text{(I.24)}$$

where

P' = any one of $N!$ operators that permute the variables $\mathbf{r}_1'$, $\mathbf{r}_2'$, $\cdots$, $\mathbf{r}_N'$, (I.25)

and

$$\mathcal{C}_{P'} = 1 \quad \text{for even permutations } P', \qquad \mathcal{C}_{P'} = -1 \quad \text{for odd permutations } P'. \quad \text{(I.26)}$$

Equations (I.23) and (I.24) are proved in Appendix B.

Starting from U_l one can construct W_l from (I.6). Equation (I.23) then enables one to compute W_l^S which in turn leads to a computation of U_l^S through (I.12). The details of these procedures appear in Appendix C. Here we only state the results as:

Rule A.—To calculate U_l^S we first distribute the l integers 1, 2, $\cdots l$ into m_α groups each containing α integers, with $\sum_\alpha m_\alpha \alpha = l$. Such a grouping may be represented as follows:

$$\{(a)(b)\cdots\}\{(cd)(ef)\cdots\}\{(ghi)\cdots\}\cdots, \quad \text{(I.27)}$$

where a, b, c, $\cdots$ are the various integers. In the first curly bracket there are m_1 round brackets with one integer in each ($m_1=0$, 1, $2\cdots$), and in the second curly bracket there are m_2 round brackets with two integers in each ($m_2=0$, 1, $2\cdots$), etc. Within each round bracket the integers are arranged in ascending order. Within each curly bracket the round brackets are arranged such that their first integers follow an ascending sequence.

We then form the sum

$$\sum\{\langle\mathfrak{a}'|U_1|a\rangle\langle\mathfrak{b}'|U_1|b\rangle\cdots\}\times\{\langle\mathfrak{c}',\mathfrak{d}'|U_2|c,d\rangle\langle\mathfrak{e}',\mathfrak{f}'|U_2|e,f\rangle\cdots\}\cdots, \quad (\text{I.28})$$

where $\mathfrak{a}'$, $\mathfrak{b}'$, $\cdots\mathfrak{c}'$, $\mathfrak{d}'$, $\mathfrak{e}'$, $\mathfrak{f}'$, $\cdots$ is any permutation of the coordinates $1'$, $2'\cdots l'$. The summation in (I.28) extends over all such permutations of $1'$, $2'\cdots l'$ which satisfy the condition [see examples (1) and (3) below] that upon putting $\mathbf{r}_i=\mathbf{r}_i'$ (all i), the summand cannot be written as a product of two factors, one of which depends only on some, but not all, of the coordinates $\mathbf{r}_1$, $\mathbf{r}_2$, $\cdots\mathbf{r}_l$, while the other depends only on the rest of these coordinates. We then sum up all expressions (I.28) over the different groupings (I.27). This total sum is equal to U_l^S.

Rule B.—To calculate U_l^A we proceed in exactly the same way as rule A, with only the following change: we replace (I.28) by

$$\sum\mathfrak{C}\{\langle\mathfrak{a}'|U_1|a\rangle\langle\mathfrak{b}'|U_1|b\rangle\cdots\}\times\{\langle\mathfrak{c}',\mathfrak{d}'|U_2|c,d\rangle\cdots\}\cdots, \quad (\text{I.29})$$

where

$$\mathfrak{C}=+1 \quad \text{if the permutation} \begin{pmatrix} a & b & c & d & \cdots \\ \mathfrak{a} & \mathfrak{b} & \mathfrak{c} & \mathfrak{d} & \cdots \end{pmatrix} \text{ is even,}$$

and

$$\mathfrak{C}=-1 \quad \text{if it is odd.}$$

The meaning of these rules is actually quite simple even though their statements appear to be so long. We quote a few examples.

Example 1:

$$U_2^S=\langle 2'|U_1|1\rangle\langle 1'|U_1|2\rangle+\langle 1',2'|U_2|1,2\rangle+\langle 2',1'|U_2|1,2\rangle.$$

The term $\langle 1'|U_1|1\rangle\langle 2'|U_1|2\rangle$ is not included because when

$$\mathbf{r}_1=\mathbf{r}_1', \quad \mathbf{r}_2=\mathbf{r}_2'$$

it splits into two factors, one of which depends only on $\mathbf{r}_1$, the other only on $\mathbf{r}_2$.

Example 2:

$$U_2^A=-\langle 2'|U_1|1\rangle\langle 1'|U_1|2\rangle+\langle 1',2'|U_2|1,2\rangle-\langle 2',1'|U_2|1,2\rangle.$$

Example 3:

A term like

$$\langle 2'|U_1|5\rangle\langle 1',6'|U_2|1,8\rangle\langle 5',3'|U_2|2,3\rangle\langle 8',7',4'|U_3|4,6,7\rangle$$

is not to be included in U_8^S because upon putting $\mathbf{r}_i=\mathbf{r}_i'$ (all i) the first and third factors together depend only on $\mathbf{r}_2$, $\mathbf{r}_3$, and $\mathbf{r}_5$ while the other two together only on $\mathbf{r}_1$, $\mathbf{r}_4$, $\mathbf{r}_6$, $\mathbf{r}_7$, and $\mathbf{r}_8$.

Example 4:

It is easy to see that for the case of Bose-Einstein statistics the combination

$$\langle 1',\cdots,l'|\Upsilon_l^S|1,\cdots,l\rangle\equiv\sum_{P'}P'\langle 1',\cdots,l'|U_l|1,\cdots,l\rangle \quad (\text{I.30})$$

always occurs instead of U_l alone. By introducing (I.30) one could simplify the formulas for U_l^S. Developments along these lines have been pursued and led to calculations of the transition point in a Bose-Einstein gas with interactions. These developments will be presented in a later paper.

Example 5:

Similarly, for the case of Fermi-Dirac statistics, the combination

$$\langle 1',\cdots,l'|\Upsilon_l^A|1,\cdots,l\rangle\equiv\sum_{P'}\mathfrak{C}_{P'}P'\langle 1',\cdots,l'|U_l|1,\cdots,l\rangle \quad (\text{I.31})$$

always occurs instead of U_l alone.

Example 6:

For free particles, using (I.20), one sees that U_l^S is equal to a sum of products of l U_1 functions. It is easy to prove that there are $(l-1)!$ terms in the sum. Equation (I.14) therefore leads to

$$b_l^S(\Omega)$$
$$=l^{-1}\Omega^{-1}\int\langle 1|U_1|2\rangle\langle 2|U_1|3\rangle\langle 3|U_1|4\rangle\cdots\langle l|U_1|1\rangle d^{3l}r$$
$$=l^{-1}\Omega^{-1}\,\text{trace}\,(U_1)^l.$$

Now by (I.16) the momentum representation of U_1 is

$$\langle\mathbf{k}'|U_1|\mathbf{k}\rangle=\delta_{\mathbf{k}\mathbf{k}'}\exp(-\beta\mathbf{k}^2). \quad (\text{I.32})$$

Hence

$$b_l^S(\Omega)=l^{-1}\Omega^{-1}\sum_{\mathbf{k}}\exp(-l\beta\mathbf{k}^2).$$

As $\Omega\to\infty$,

$$b_l^S(\Omega)\to l^{-1}(8\pi^3)^{-1}\int\exp(-l\beta\mathbf{k}^2)d^3k=\lambda^{-3}l^{-\frac{5}{2}}, \quad (\text{I.33})$$

which agrees with well-known results. One obtains similarly

$$b_l^A(\Omega)\to(-1)^{l-1}\lambda^{-3}l^{-\frac{5}{2}}. \quad (\text{I.34})$$

4. U_l IN TERMS OF THE BINARY KERNEL

The functions U_l will be expressed in this section in terms of a function B, called the binary kernel, which is calculable from a solution of the two-particle problem.

We treat W_N, U_N as *operators* and write

$$W_N(\beta)=\exp(-\beta H_N). \quad (\text{I.35})$$

Here we have explicitly indicated the β dependence of W_N. Writing $H_N=T_N+V_N$, where T_N and V_N are, respectively, the operators for the kinetic and potential energies, one notices that

$$W_N{}^0(\beta)\equiv\exp(-\beta T_N)=\prod_{i=1}^{N} w(\beta;i),$$

where

$$w(\beta;i)\equiv\exp(\beta\nabla_i{}^2). \tag{I.36}$$

The explicit form of $w(\beta;1)=\langle 1'|W_1|1\rangle$ is given by (I.16). Thus $W_N{}^0(\beta)$ is a product of N operators each of which operates on the coordinates of one particle. If V is finite, one can expand W_N into an exponential series in powers of V:

$$W_N(\beta)=W_N{}^0(\beta)+\int_0^\beta W_N{}^0(\beta-\beta')(-V_N)W_N{}^0(\beta')d\beta'$$
$$+\int_0^\beta d\beta'\int_0^{\beta'} d\beta''\, W_N{}^0(\beta-\beta')(-V_N)$$
$$\times W_N{}^0(\beta'-\beta'')(-V_N)W_N{}^0(\beta'')+\cdots. \tag{I.37}$$

If V is $+\infty$ for some configurations, this series ceases to be meaningful. For the time being we regard V as finite everywhere, and shall allow for the possibility of V going to $+\infty$ *after* some rearrangements of terms to be discussed later.

It is of great convenience to represent the sum in (I.37) by diagrams. We shall represent $W_N(\beta)$ as a sum of operators, each corresponding to a different diagram which consists of N vertical lines ii' connecting the points i with i' ($i=1, \cdots, N$). The points i are all on the same horizontal base level. All the vertical lines ii' are of the same length β and are linked by some horizontal links, *no two of which are at the same height* (i.e., the vertical distances between the horizontal base level and different links are different).

In Fig. 1 we give some examples of the diagrams for W_1, W_2, and W_3. To specify a diagram, one does not specify the exact heights of the horizontal links (since they are to be integrated over), only the vertical sequence in which they are drawn. Thus, for example, in Fig. 1 the sixth and the seventh diagrams for $W_3(\beta)$ are counted as different diagrams.

To obtain the operator that corresponds to a diagram, one proceeds as follows:

A line segment of length γ along the vertical line ii' stands for the operator $w(\gamma;i)=\exp(\gamma\nabla_i{}^2)$. A horizontal link between ii' and jj' represents the operator $-V(\mathbf{r}_i-\mathbf{r}_j)d\beta'$ where β' is the height of the link above the base line. Multiplying all the operators represented by all the vertical line segments and by the horizontal links, and integrating over the heights β' of the various horizontal links, one obtains the operator represented by the diagram. Two important further rules must be followed:

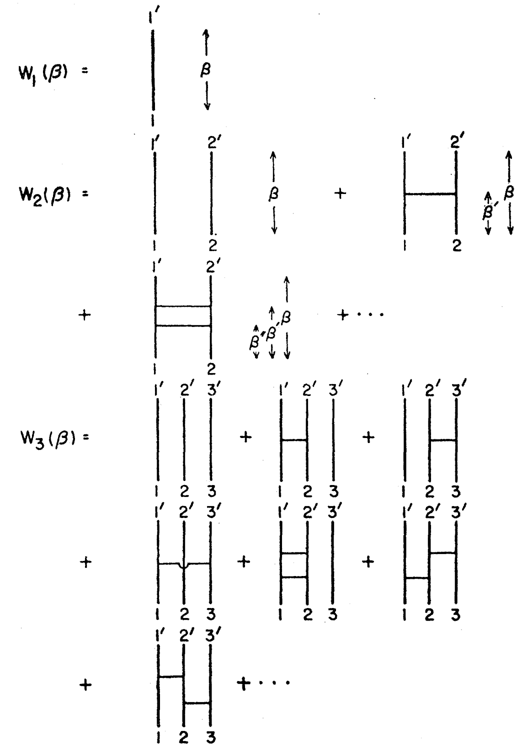

FIG. 1. Diagram representation of W_N as a power series in V. W_3 has altogether 9 diagrams with 2 horizontal links, 27 diagrams with 3 horizontal links, etc. The operators that correspond to these diagrams are given by Eqs. (I.38), (I.39), and (I.40).

(a) The order in which the operators stand must be such that those representing line elements lower down in the diagram stand to the right of those representing line elements higher up in the diagram.

(b) The limits of integration of the heights β' of the horizontal links are defined by the conditions that $\beta\geqq\beta'\geqq0$, and that the relative height of any two links remain of the same sign within the limits of integration as in the diagram.

Explicitly, the diagram for $W_1(\beta)$ in Fig. 1 corresponds to the operator

$$W_1(\beta)=w(\beta;1). \tag{I.38}$$

The first three diagrams for $W_2(\beta)$ in Fig. 1 correspond to, respectively, the first three terms in the sum

$$W_2(\beta)=w(\beta;1)w(\beta;2)+\int_0^\beta w(\beta-\beta';1)w(\beta-\beta';2)$$
$$\times(-V_{12})w(\beta';1)w(\beta';2)d\beta'+\int_0^\beta d\beta'\int_0^{\beta'} d\beta''$$
$$\times w(\beta-\beta';1)w(\beta-\beta';2)(-V_{12})w(\beta'-\beta'';1)$$
$$\times w(\beta'-\beta'';2)(-V_{12})w(\beta'';1)w(\beta'';2)+\cdots. \tag{I.39}$$

Similarly, the first three diagrams for $W_3(\beta)$ in Fig. 1 correspond, respectively, to the first three terms in the

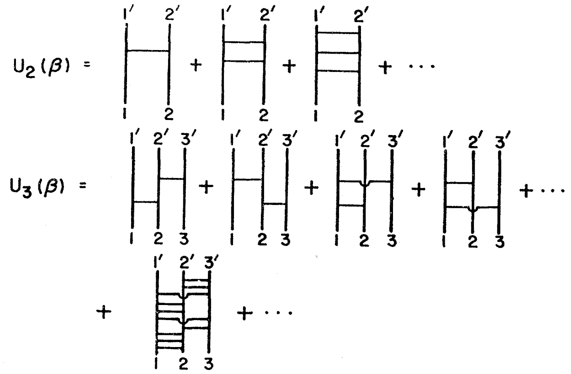

FIG. 2. Diagram representation of U_N as a power series in V. U_3 has altogether 6 diagrams with 2 horizontal links and 24 diagrams with 3 horizontal links, etc. [See Eq. (I.42).]

following sum:

$$W_3(\beta)=w(\beta;1)w(\beta;2)w(\beta;3)+\left[\int_0^\beta w(\beta-\beta';1)\right.$$
$$\left.\times w(\beta-\beta';2)(-V_{12})w(\beta';1)w(\beta';2)d\beta'\right]w(\beta;3)$$
$$+w(\beta;1)\left[\int_0^\beta w(\beta-\beta';2)w(\beta-\beta';3)(-V_{23})\right.$$
$$\left.\times w(\beta';2)w(\beta';3)d\beta'\right]+\cdots. \quad (I.40)$$

In terms of these diagrams, Eq. (I.37) becomes

$$W_N(\beta)=\sum(\text{all different diagrams with the parameter } \beta \text{ and with } N \text{ particles}). \quad (I.41)$$

As is clear from the examples illustrated above, some of these diagrams may have unconnected parts. The unconnected parts of a diagram represent commuting operators whose product is the operator corresponding to the whole diagram.

Let us define a "connected diagram" to be one in which all parts are connected through the vertical lines and the horizontal links. By comparing Eq. (I.6) with Eqs. (I.39) and (I.40) (or with their corresponding diagrams in Fig. 1), one finds that U_2 is the sum of all "connected diagrams" in $W_2(\beta)$ and U_3 is the sum of all "connected diagrams" in $W_3(\beta)$. This property is illustrated in Fig. 2.

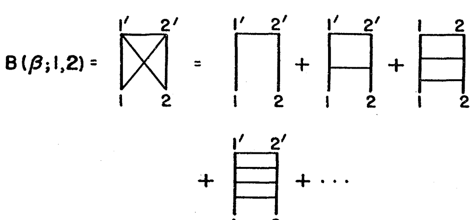

FIG. 3. Diagram representation of B.

In fact, one sees in general that

$$U_N(\beta)=\sum(\text{all different "connected diagrams" with the parameter } \beta \text{ and with } N \text{ particles}). \quad (I.42)$$

A comparison of (I.41) and (I.42) shows that the diagrams that contribute to $W_N(\beta)$ but not to $U_N(\beta)$ are the unconnected ones which are grouped in the Ursell expansion (I.6) into products of U_l with values of $l<N$. We shall see in the next section and in Appendix E that the connectedness of the diagrams in $U_N(\beta)$ also determines the behavior of $U_N(\beta)$ as the positions of the particles become far distant from each other.

It is convenient to give an explicit operator form for U_2. Using (I.6) and (I.35), we find

$$U_2(\beta)=\exp(-\beta H_2)-\exp(+\beta\nabla_1^2)\exp(+\beta\nabla_2^2). \quad (I.43)$$

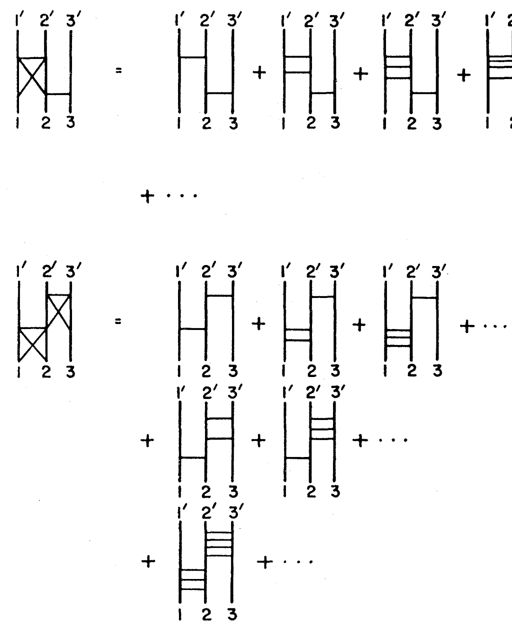

FIG. 4. Examples of diagrams which contain B as part of their structure.

We shall now define the binary kernel $B(\beta;1,2)$:

$$B(\beta;1,2)\equiv(-V_{12})W_2(\beta)=(-V_{12})\exp(-\beta H_2). \quad (I.44)$$

From (I.43) one obtains, by differentiating with respect to β,

$$B(\beta;1,2)=\frac{\partial U_2(\beta)}{\partial\beta}-(\nabla_1^2+\nabla_2^2)U_2(\beta). \quad (I.45)$$

It is important to notice that by using the solutions of the two-body problem (in a box Ω) one can compute $\exp(-\beta H_2)$. Equations (I.43) and (I.45) then lead to a computation of $U_2(\beta)$ and $B(\beta;1,2)$. Furthermore, these two equations do not contain V explicitly. Therefore, the explicit form of $B(\beta;1,2)$ can be evaluated even if $V=+\infty$ for some spatial configurations of $\mathbf{r}_1$ and $\mathbf{r}_2$. The example of hard spheres will be given in a later section.

Substituting the diagrams for W_2 in Fig. 1 into (I.44), one is led to the representation of B in terms of the diagrams of Fig. 3. The top horizontal links in the last four diagrams represent factors $(-V_{12})$. With this definition it is clear that any group of graphs with a part that has the same form as these diagrams can be summed to yield a factor B. In Fig. 4 we give two such examples.

We have seen before that U_N is equal to a sum of connected diagrams. The sum can be rearranged and grouped together in the same manner as the two examples in Fig. 4. One then obtains U_N as a sum of diagrams in which only B appears with no isolated horizontal links. In Fig. 5 we express $U_2(\beta)$, $U_3(\beta)$, etc. in terms of sums of such diagrams.

From these diagrams the explicit form of U_l in terms of the binary kernel B can be readily written down:

$$U_2(\beta)=\int_0^\beta d\beta'\, w(\beta-\beta';1)w(\beta-\beta';2)B(\beta';1,2), \quad \text{(I.46)}$$

$$\begin{aligned}U_3(\beta)=&\int_0^\beta d\beta'\int_0^{\beta'} d\beta''\, w(\beta-\beta'';1)w(\beta-\beta';2)\\&\times w(\beta-\beta';3)B(\beta'-\beta'';2,3)B(\beta'';1,2)w(\beta'';3)\\&+\int_0^\beta d\beta'\int_0^{\beta'} d\beta''\, w(\beta-\beta';1)w(\beta-\beta';2)\\&\times w(\beta-\beta'';3)B(\beta'-\beta'';1,2)B(\beta'';2,3)w(\beta'';1)\\&+\text{four other terms of order } B^2\\&\qquad+\text{terms of higher orders in } B. \quad \text{(I.47)}\end{aligned}$$

$$\begin{aligned}U_4(\beta)=&\int_0^\beta d\beta'\int^{\beta'} d\beta''\int_0^{\beta''} d\beta'''\, w(\beta-\beta';1)\\&\times w(\beta-\beta''';2)w(\beta-\beta'';3)w(\beta-\beta';4)\\&\times B(\beta'-\beta'';1,4)B(\beta''-\beta''';3,4)\\&\times B(\beta''';2,3)w(\beta'';1)w(\beta''';4)\\&+95 \text{ other terms of order } B^3\\&\qquad+\text{terms of higher order in } B. \quad \text{(I.48)}\end{aligned}$$

$$U_5(\beta)=\cdots. \quad \text{(I.49)}$$

In (I.47) the first and the second operator on the right-hand side represent, respectively, the first and the second diagram in the corresponding sum for U_3 in Fig. 5, and the first operator on the right-hand side of (I.48) represents the corresponding first diagram for U_4 in Fig. 5.

These equations express U_l for $l\geq 3$ as a sum of integrals of products of w and B. Now B vanishes for free particles. It characterizes the perturbation on W_2 due to the interactions. The expansion in Fig. 5 and in (I.47), (I.48), (I.49) for U_l are thus expansions in

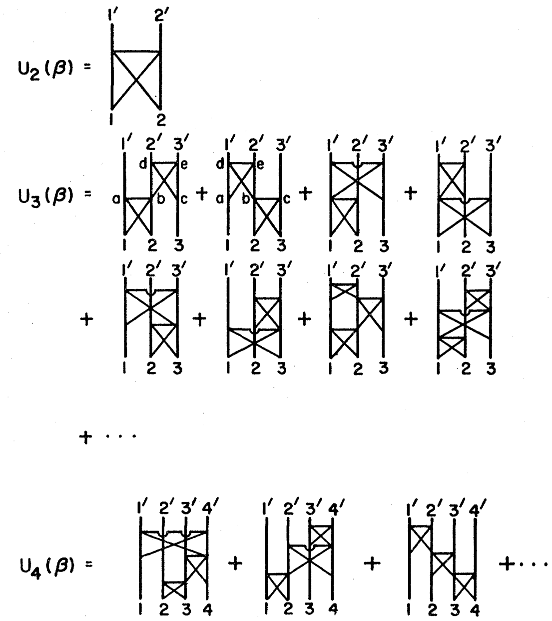

FIG. 5. Diagram representation of U_N in terms of the binary kernel B. In these diagrams there is no horizontal link (which corresponds to V). The vertical lines are all connected through structures representing B. The operators that correspond to these diagrams are given by Eqs. (I.46)–(I.48).

terms of increasingly higher order effects of such a perturbation. The convergence of such expansions is not clearly understood by the authors. It is, however, hoped that for interactions for which three-particle bound states do not exist these expansions do converge.

Equations (I.46)–(I.48) are operator equations. For illustration we give the explicit matrix element of, say, $U_3(\beta)$ between the states $\langle 1',2',3'|$ and $|1,2,3\rangle$ in the coordinate representation. From (I.47) we obtain

$$\begin{aligned}&\langle \mathbf{r}_1',\mathbf{r}_2',\mathbf{r}_3'|U_3|\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3\rangle\\&=\int_0^\beta d\beta'\int_0^{\beta'} d\beta''\int d^3\mathbf{r}_a d^3\mathbf{r}_b d^3\mathbf{r}_c d^3\mathbf{r}_d d^3\mathbf{r}_e\\&\quad\times\langle \mathbf{r}_1'|W_1(\beta-\beta'')|\mathbf{r}_a\rangle\langle \mathbf{r}_2'|W_1(\beta-\beta')|\mathbf{r}_d\rangle\\&\quad\times\langle \mathbf{r}_3'|W_1(\beta-\beta')|\mathbf{r}_e\rangle\langle \mathbf{r}_d,\,\mathbf{r}_e|B(\beta'-\beta'')|\mathbf{r}_b,\mathbf{r}_c\rangle\\&\quad\times\langle \mathbf{r}_a,\mathbf{r}_b|B(\beta'')|\mathbf{r}_1,\mathbf{r}_2\rangle\langle \mathbf{r}_c|W_1(\beta'')|\mathbf{r}_3\rangle\\&\quad+\int_0^\beta d\beta'\int_0^{\beta'} d\beta''\int d^3\mathbf{r}_a\cdots\\&\quad\times d^3\mathbf{r}_e\langle \mathbf{r}_1'|W_1(\beta-\beta')|\mathbf{r}_d\rangle\langle \mathbf{r}_2'|W_1(\beta-\beta')|\mathbf{r}_e\rangle\\&\quad\times\langle \mathbf{r}_3'|W_1(\beta-\beta'')|\mathbf{r}_c\rangle\langle \mathbf{r}_d,\,\mathbf{r}_e|B(\beta'-\beta'')|\mathbf{r}_a,\,\mathbf{r}_b\rangle\\&\quad\times\langle \mathbf{r}_b,\mathbf{r}_c|B(\beta'')|\mathbf{r}_2,\mathbf{r}_3\rangle\langle \mathbf{r}_a|W_1(\beta'')|\mathbf{r}_1\rangle+\cdots. \quad \text{(I.50)}\end{aligned}$$

where the first two terms again correspond to the first two diagrams for U_3 in Fig. 5. The five corners in each of these two diagrams are denoted by a, b, c, d, and e.

In (I.50) we denote the spatial coordinates of these five corners by $\mathbf{r}_a$, $\mathbf{r}_b$, $\cdots\mathbf{r}_e$ and the heights of the horizontal lines ab, de by β'' and β', respectively.

5. THE LIMIT $\Omega\rightarrow\infty$. MOMENTUM REPRESENTATION

The results of the last three sections hold for arbitrary but finite values of Ω. If one starts with the Hamiltonian (I.1), but without the periodicity boundary condition, one is dealing[7] with the case $\Omega=\infty$. One can then still define the functions W_N, W_N^S, and W_N^A by (I.4), (I.11), and (I.15). Also the definitions (I.6), (I.12) for the U_l, U_l^S, and U_l^A functions are unchanged. All the discussions and results of Secs. 3 and 4 apply to the case $\Omega=\infty$ as well as to the case of finite Ω. However, the discussions in Sec. 2 concerning the partition function, the grand partition function, and the thermodynamical behavior of the system cannot apply to a system with $\Omega=\infty$ (for which the partition function is clearly ∞).

To emphasize the dependence on Ω we shall in the rest of this section add the inferior indices Ω and ∞ to indicate the cases of finite Ω and infinite Ω, respectively.

One can rewrite (I.10) in the form [to be proved in Appendix D]:

$$b_l(\Omega)=(l!)^{-1}\int_\Omega\langle 0,\mathbf{r}_2,\mathbf{r}_3,\cdots\mathbf{r}_l|U_{l\Omega}|0,\mathbf{r}_2,\mathbf{r}_3,\cdots\mathbf{r}_l\rangle \times d^3r_2d^3r_3\cdots d^3r_l. \quad \text{(I.51)}$$

Similarly one has identical equations for b_l^S and b_l^A with $U_{l\Omega}^S$ and $U_{l\Omega}^A$ replacing $U_{l\Omega}$. In (I.51) the region of integration of $\mathbf{r}_2$, $\mathbf{r}_3$, $\cdots\mathbf{r}_l$ is the box

$$\tfrac{1}{2}L\geqq x_i\geqq -\tfrac{1}{2}L,\quad \tfrac{1}{2}L\geqq y_i\geqq -\tfrac{1}{2}L,$$
$$\tfrac{1}{2}L\geqq z_i\geqq -\tfrac{1}{2}L;\quad i\geqq 2;\quad (\Omega=L^3). \quad \text{(I.52)}$$

It will be demonstrated in Appendix E that as $\Omega\rightarrow\infty$, the matrix elements of all the $W_{N\Omega}$, $U_{N\Omega}$, $W_{N\Omega}^S$, etc., operators for fixed $\mathbf{r}_1$, $\mathbf{r}_2$, $\cdots\mathbf{r}_N$ and $\mathbf{r}_1'$, $\mathbf{r}_2'$, $\cdots\mathbf{r}_N'$ approach the matrix elements of the corresponding operators at $\Omega=\infty$. Furthermore, it will also be demonstrated there that from (I.51) one obtains, as $\Omega\rightarrow\infty$,

$$b_l(\Omega)\rightarrow b_l(\infty)$$
$$\equiv(l!)^{-1}\int\langle 0,\mathbf{r}_2,\mathbf{r}_3,\cdots\mathbf{r}_l|U_{l\infty}|0,\mathbf{r}_2,\cdots\mathbf{r}_l\rangle \times d^3r_2d^3r_3\cdots d^3r_l,$$

$$b_l^S(\Omega)\rightarrow b_l^S(\infty)$$
$$\equiv(l!)^{-1}\int\langle 0,\mathbf{r}_2,\mathbf{r}_3,\cdots\mathbf{r}_l|U_{l\infty}^S|0,\mathbf{r}_2,\mathbf{r}_3,\cdots\mathbf{r}_l\rangle \times d^3r_2d^3r_3\cdots d^3r_l, \quad \text{(I.53)}$$

$$b_l^A(\Omega)\rightarrow b_l^A(\infty)$$
$$\equiv(l!)^{-1}\int\langle 0,\mathbf{r}_2,\mathbf{r}_3,\cdots\mathbf{r}_l|U_{l\infty}^A|0,\mathbf{r}_2,\cdots\mathbf{r}_l\rangle \times d^3r_2d^3r_3\cdots d^3r_l,$$

the limits of integration being $-\infty$ to ∞. The U_l functions for $\Omega=\infty$ are therefore useful for calculating the limits of b_l, b_l^S, and b_l^A as $\Omega\rightarrow\infty$.

To summarize the results of these sections: One has a program[8] of computing the limits $b_l(\infty)$, $b_l^S(\infty)$, and $b_l^A(\infty)$ using exclusively quantities defined for $\Omega=\infty$. The method is usable even if the two-body interaction $V(r)$ is equal to $+\infty$ for some values of $\mathbf{r}$. The quantities to be computed in successive steps in the program are: first, $W_{2\infty}$ by solving the two-body problem; second, B_∞ through (I.43) and (I.45); third, $U_{l\infty}$ through (I.46)–(I.49); fourth, $U_{l\infty}^S$ and $U_{l\infty}^A$ through the rules A and B of Sec. 3; and last, $b_l(\infty)$, $b_l^S(\infty)$, and $b_l^A(\infty)$ through (I.53).

In carrying out this program it is sometimes convenient to use the momentum representation. One notices first that (I.43), (I.45), and (I.46)–(I.49) as operator equations are of course valid in any representation. As to rules A and B in Sec. 3, if one understands 1, 2, $\cdots$ to mean $\mathbf{k}_1$, $\mathbf{k}_2$, $\cdots$ the rules remain valid and in fact give the momentum representation of U_l^S and U_l^A in terms of those of U_l. Consequently (I.43), (I.45)–(I.49), and rules A and B are applicable to both coordinate and momentum representations, and to the case of $\Omega=$finite and $\Omega=\infty$.

To compute $b_l(\infty)$ etc. from the matrix elements of U_l in momentum representation, one writes

$$\langle\mathbf{k}_1',\mathbf{k}_2'\cdots\mathbf{k}_l'|U_{l\infty}|\mathbf{k}_1,\mathbf{k}_2\cdots\mathbf{k}_l\rangle \equiv\delta^3(\textstyle\sum\mathbf{k}_\alpha-\sum\mathbf{k}_\alpha')\langle\mathbf{k}_1'\cdots\mathbf{k}_l'|u_l|\mathbf{k}_1\cdots\mathbf{k}_l\rangle,$$
$$\langle\mathbf{k}_1',\mathbf{k}_2'\cdots\mathbf{k}_l'|U_{l\infty}^S|\mathbf{k}_1,\mathbf{k}_2\cdots\mathbf{k}_l\rangle \equiv\delta^3(\textstyle\sum\mathbf{k}_\alpha-\sum\mathbf{k}_\alpha')\langle\mathbf{k}_1'\cdots\mathbf{k}_l'|u_l^S|\mathbf{k}_1\cdots\mathbf{k}_l\rangle, \quad \text{(I.54)}$$
$$\langle\mathbf{k}_1',\mathbf{k}_2'\cdots\mathbf{k}_l'|U_{l\infty}^A|\mathbf{k}_1,\mathbf{k}_2\cdots\mathbf{k}_l\rangle \equiv\delta^3(\textstyle\sum\mathbf{k}_\alpha-\sum\mathbf{k}_\alpha')\langle\mathbf{k}_1'\cdots\mathbf{k}_l'|u_l^A|\mathbf{k}_1,\cdots\mathbf{k}_l\rangle.$$

The presence of the δ function is a consequence of the conservation of momentum for the Hamiltonian (I.1). The functions u_l etc. are defined through (I.54) only for those values of $\mathbf{k}_\alpha'$ and $\mathbf{k}_\alpha$ which satisfy $\sum\mathbf{k}_\alpha'=\sum\mathbf{k}_\alpha$. Now for $\Omega=\infty$

$$\langle\mathbf{k}_1\cdots\mathbf{k}_l|\mathbf{r}_1\cdots\mathbf{r}_l\rangle=(8\pi^3)^{-l/2}\exp\left[-\sum_1^l i\mathbf{k}_\alpha\cdot\mathbf{r}_\alpha\right].$$

Hence

$$\langle\mathbf{r}_1'\cdots\mathbf{r}_l'|U_{l\infty}|\mathbf{r}_1\cdots\mathbf{r}_l\rangle=\int\langle\mathbf{k}_1'\cdots\mathbf{k}_l'|U_{l\infty}|\mathbf{k}_1\cdots\mathbf{k}_l\rangle \times d^{3l}k'd^{3l}k(8\pi^3)^{-l}\exp(i\textstyle\sum\mathbf{k}_\alpha'\cdot\mathbf{r}_\alpha'-i\sum\mathbf{k}_\alpha\cdot\mathbf{r}_\alpha).$$

[7] This approach to the problem at $\Omega=\infty$ is along the lines of Dirac's representation theory [P. A. M. Dirac, *The Principles of Quantum Mechanics* (Oxford University Press, Oxford, 1947)]. An alternative way of defining the W_N functions for $\Omega=\infty$ appears in Appendix E.

[8] The question of whether

$$\lim_{\Omega\rightarrow\infty}\sum b_l(\Omega)z^l=\sum b_l(\infty)z^l$$

is not discussed here. However, see C. N. Yang and T. D. Lee, Phys. Rev. **87**, 404 (1952).

Using (I.53) and (I.54), one obtains

$$b_l(\infty)=(l!8\pi^3)^{-1}\int\langle\mathbf{k}_1\cdots\mathbf{k}_l|u_l|\mathbf{k}_1\cdots\mathbf{k}_l\rangle d^{3l}k. \quad (\text{I.55})$$

Similarly,

$$b_l{}^S(\infty)=(l!8\pi^3)^{-1}\int\langle\mathbf{k}_1\cdots\mathbf{k}_l|u_l{}^S|\mathbf{k}_1\cdots\mathbf{k}_l\rangle d^{3l}k,$$

and

$$b_l{}^A(\infty)=(l!8\pi^3)^{-1}\int\langle\mathbf{k}_1\cdots\mathbf{k}_l|u_l{}^A|\mathbf{k}_1\cdots\mathbf{k}_l\rangle d^{3l}k. \quad (\text{I.56})$$

6. BINARY KERNEL B FOR HARD-SPHERE INTERACTION

To calculate B for $\Omega=\infty$ and for a central potential V, one first introduces center-of-mass and relative coordinates:

$$\mathbf{R}=\tfrac{1}{2}(\mathbf{r}_1+\mathbf{r}_2),\quad \mathbf{r}=\mathbf{r}_1-\mathbf{r}_2. \quad (\text{I.57})$$

The Jacobian of the transformation is equal to unity. Spherical coordinates r, θ, ϕ will be introduced to replace the vector $\mathbf{r}$. Now

$$H_2=-\nabla_1{}^2-\nabla_2{}^2+V(r)=H_R+H_r,$$

where

$$H_R=-\tfrac{1}{2}\nabla_R{}^2\quad\text{and}\quad H_r=-2\nabla_r{}^2+V(r). \quad (\text{I.58})$$

Let the normalized bound state solution in the center-of-mass system of the two particles be $\psi_i(\mathbf{r})$ $(i=1, 2, \cdots)$ so that

$$H_r\psi_i(\mathbf{r})=E_i\psi_i(\mathbf{r})$$

and

$$\int|\psi_i(\mathbf{r})|^2d^3r=1. \quad (\text{I.59})$$

Also let the continuum solutions be ψ_{klm} which satisfy

$$\psi_{klm}=(2\pi^{-1})^{\frac{1}{2}}r^{-1}\mathcal{R}_{kl}(r)Y_{lm}(\theta,\phi),$$
$$H\psi_{klm}=2k^2\psi_{klm},$$

and

$$\mathcal{R}_{kl}\rightarrow\sin(kr-\tfrac{1}{2}l\pi+\delta_{kl})\quad\text{as}\quad r\rightarrow\infty. \quad (\text{I.60})$$

The spherical harmonics Y_{lm} are here defined so that

$$\int_0^\pi\sin\theta d\theta\int_0^{2\pi}|Y_{lm}|^2d\phi=1.$$

The normalization condition (I.60) insures[9] that

$$\int\psi_{k'l'm'}{}^*(\mathbf{r})\psi_{klm}(\mathbf{r})d^3\mathbf{r}=\delta_{l',l}\delta_{m',m}\delta(k'-k). \quad (\text{I.61})$$

Therefore

$$\langle\mathbf{r}'|\exp(-\beta H)|\mathbf{r}\rangle=\textstyle\sum_i\psi_i(\mathbf{r}')\psi_i{}^*(\mathbf{r})\exp(-\beta E_i)$$
$$+\sum_{lm}\int_0^\infty dk\,\psi_{klm}(\mathbf{r}')\psi_{klm}{}^*(\mathbf{r})\exp(-2\beta k^2). \quad (\text{I.62})$$

[9] In the sense of the transformation theory of Dirac (see reference 7).

The last term can be written as

$$\sum_l 2(\pi)^{-1}\int_0^\infty dk(rr')^{-1}\mathcal{R}_{kl}(r')\mathcal{R}_{kl}{}^*(r)$$
$$\times\exp(-2\beta k^2)\sum_m Y_{lm}(\theta',\phi')Y_{lm}{}^*(\theta,\phi)$$
$$=\sum_l(2l+1)(2\pi^2rr')^{-1}P_l(\cos\Theta)$$
$$\times\int_0^\infty dk\,\mathcal{R}_{kl}(r')\mathcal{R}_{kl}{}^*(r)\exp(-2\beta k^2), \quad (\text{I.63})$$

where

$$P_l(\xi)=\frac{1}{2^l l!}\frac{d^l}{d\xi^l}(\xi^2-1)^l,$$

and

$$\cos\Theta=(rr')^{-1}\mathbf{r}\cdot\mathbf{r}'.$$

To complete the calculation of W_2 it is also necessary to compute the operator $\exp(-\beta H_R)=\exp(+\frac{1}{2}\beta\nabla_R{}^2)$. The eigenvalues and eigenfunctions of $\nabla_R{}^2$ are $-K^2$ and $(8\pi^3)^{-\frac{1}{2}}\exp(i\mathbf{K}\cdot\mathbf{R})$. Hence

$$\langle\mathbf{R}'|\exp(\tfrac{1}{2}\beta\nabla_R{}^2)|\mathbf{R}\rangle$$
$$=(8\pi^3)^{-1}\int d^3K\exp[-\tfrac{1}{2}\beta\mathbf{K}^2+i\mathbf{K}\cdot(\mathbf{R}'-\mathbf{R})]$$
$$=8^{\frac{1}{2}}\lambda^{-3}\exp[-(\mathbf{R}'-\mathbf{R})^2/(2\beta)].$$

Collecting all terms we thus obtain a general formula for the coordinate representation of W_2 for the case $\Omega=\infty$ and V=central potential:

$$\langle\mathbf{r}_1',\mathbf{r}_2'|\exp(-\beta H_2)|\mathbf{r}_1,\mathbf{r}_2\rangle$$
$$=8^{\frac{1}{2}}\lambda^{-3}\exp[-(\mathbf{r}_1'+\mathbf{r}_2'-\mathbf{r}_1-\mathbf{r}_2)^2/(8\beta)]$$
$$\times\Big\{\textstyle\sum_i\psi_i(\mathbf{r}')\psi_i{}^*(\mathbf{r})\exp(-\beta E_i)$$
$$+\textstyle\sum_l(2l+1)(2\pi^2rr')^{-1}P_l(\cos\Theta)$$
$$\times\int_0^\infty dk\mathcal{R}_{kl}(r')\mathcal{R}_{kl}{}^*(r)\exp(-2\beta k^2)\Big\}. \quad (\text{I.64})$$

To obtain U_2 one subtracts from this the corresponding expression for free particles. In other words, if one replaces $\mathcal{R}_{kl}(r')\mathcal{R}_{kl}{}^*(r)$ in (I.64) by

$$\mathcal{R}_{kl}(r')\mathcal{R}_{kl}{}^*(r)-[\mathcal{R}_{kl}(r')\mathcal{R}_{kl}{}^*(r)]_{\text{free}}, \quad (\text{I.65})$$

one obtains the coordinate representation of U_2.

For the hard-sphere interaction,

$$V(\mathbf{r}_1-\mathbf{r}_2)=+\infty\quad\text{for}\quad|\mathbf{r}_1-\mathbf{r}_2|\leqq a,$$
$$V(\mathbf{r}_1-\mathbf{r}_2)=0\quad\text{for}\quad|\mathbf{r}_1-\mathbf{r}_2|>a;$$

there are no bound states. Now in the integral in (I.64) the exponential factor limits the important values of k to $\lesssim\lambda^{-1}$. If $(a/\lambda)\ll1$, for these small wave numbers the effect of the hard sphere is masked by the centrifugal force in all states $l>0$. In fact, e.g., the phase shift for $l=1$ is $\delta_{kl}\cong-\frac{1}{3}(ka)^3\approx-\frac{1}{3}(a/\lambda)^3$. Neglecting such small contributions of the order of $(a/\lambda)^3$ one obtains only the contribution from the S state (i.e., $l=0$ state), for which (I.65) becomes

$$\sin(kr'-ka)\sin(kr-ka)-\sin kr'\sin kr =\tfrac{1}{2}\cos(kr'+kr)-\tfrac{1}{2}\cos(kr'+kr-2ka) \quad \text{for } r'>a \text{ and } r>a,$$

and

$$-\sin kr'\sin kr=\tfrac{1}{2}\cos(kr'+kr)-\tfrac{1}{2}\cos(kr'-kr) \quad \text{for } r'<a \text{ or } r<a.$$

The integration over k is straightforward. One obtains

$$\langle \mathbf{r}_1',\mathbf{r}_2'|U_2|\mathbf{r}_1,\mathbf{r}_2\rangle =(2\pi\lambda^4rr')^{-1}\exp[-(\mathbf{r}_1'+\mathbf{r}_2'-\mathbf{r}_1-\mathbf{r}_2)^2/(8\beta)] \times\begin{cases}\exp[-(r+r')^2/(8\beta)] -\exp[-(r+r'-2a)^2/(8\beta)] & \text{for } r>a,\ r'>a,\\ \exp[-(r+r')^2/(8\beta)] -\exp[-(r-r')^2/(8\beta)] & \text{otherwise.}\end{cases} \quad (I.66)$$

We recall that $r=|\mathbf{r}_1-\mathbf{r}_2|$, $r'=|\mathbf{r}_1'-\mathbf{r}_2'|$. To go into the momentum representation, we use

$$\langle \mathbf{k}_1',\mathbf{k}_2'|U_2|\mathbf{k}_1,\mathbf{k}_2\rangle=\int\langle \mathbf{k}_1'|\mathbf{r}_1'\rangle\langle \mathbf{k}_2'|\mathbf{r}_2'\rangle\langle \mathbf{r}_1|\mathbf{k}_1\rangle\langle \mathbf{r}_2|\mathbf{k}_2\rangle \times\langle \mathbf{r}_1',\mathbf{r}_2'|U_2|\mathbf{r}_1,\mathbf{r}_2\rangle d^3r_1d^3r_2d^3r_1'd^3r_2',$$

and

$$\langle \mathbf{r}|\mathbf{k}\rangle=(8\pi^3)^{-\frac{1}{2}}\exp(i\mathbf{k}\cdot\mathbf{r}).$$

The computation is tedious but straightforward. One first integrates over the center-of-mass coordinates $\mathbf{R}$ and $\mathbf{R}'$. Then one integrates over the angles of $\mathbf{r}$ and $\mathbf{r}'$. After the transformation

$$r+r'=\xi,\quad r-r'=\eta,$$

one integrates over ξ or over η and obtains finally

$$\begin{aligned}\langle \mathbf{k}_1',\mathbf{k}_2'|U_2|\mathbf{k}_1,\mathbf{k}_2\rangle &=[4\pi^2kk'(k^2-k'^2)]^{-1}\delta^3(\mathbf{k}_1'+\mathbf{k}_2'-\mathbf{k}_1-\mathbf{k}_2)\\ &\times\{[\sin(k+k')a][k\exp(-\beta E)-k'\exp(-\beta E')]\\ &-[\sin(k-k')a][k\exp(-\beta E)+k'\exp(-\beta E')]\\ &+\pi^{-\frac{1}{2}}2[\cos(k+k')a-\cos(k-k')a]\\ &\times[kM(\sqrt{2}\beta^{\frac{1}{2}}k)\exp(-\beta E)\\ &-k'M(\sqrt{2}\beta^{\frac{1}{2}}k')\exp(-\beta E')]\},\end{aligned} \quad (I.67)$$

where

$$k=\tfrac{1}{2}|\mathbf{k}_1-\mathbf{k}_2|,\qquad E=k_1^2+k_2^2,$$
$$k'=\tfrac{1}{2}|\mathbf{k}_1'-\mathbf{k}_2'|,\quad E'=k_1'^2+k_2'^2,$$

and

$$M(y)=\int_0^y\exp(x^2)dx. \quad (I.68)$$

For large y,

$$M(y)=[\exp(y^2)][(2y)^{-1}+(4y^3)^{-1}+\cdots] \quad (I.69)$$

asymptotically. One notices that the factor $[kk'(k^2-k'^2)]^{-1}$ does not introduce any singularities in (I.67) because the other factors vanish at $k=k'$, and at $k=0$ and $k'=0$. We can now use (I.45) to compute the binary function B. In momentum representation (I.45) assumes the form

$$\langle \mathbf{k}_1',\mathbf{k}_2'|B|\mathbf{k}_1,\mathbf{k}_2\rangle=\frac{\partial}{\partial\beta}\langle \mathbf{k}_1',\mathbf{k}_2'|U_2|\mathbf{k}_1,\mathbf{k}_2\rangle +E'\langle \mathbf{k}_1',\mathbf{k}_2'|U_2|\mathbf{k}_1,\mathbf{k}_2\rangle.$$

Using (I.67), one obtains (contributions due to S states only)

$$\begin{aligned}\langle \mathbf{k}_1',\mathbf{k}_2'|B|\mathbf{k}_1,\mathbf{k}_2\rangle &=-(\pi^2kk')^{-1}\delta^3(\mathbf{k}_1'+\mathbf{k}_2'-\mathbf{k}_1-\mathbf{k}_2)\\ &\times[\sin(k'a)][\exp(-\beta E)]\{k\cos ka-\pi^{-\frac{1}{2}}\sin ka\\ &\times[2kM(\sqrt{2}\beta^{\frac{1}{2}}k)-(2\beta)^{-\frac{1}{2}}\exp(2\beta k^2)]\}\\ &-(4\pi^2kk')^{-1}\delta(\beta)\delta^3(\mathbf{k}_1+\mathbf{k}_2-\mathbf{k}_1'-\mathbf{k}_2')\\ &\times[(k-k')^{-1}\sin(k-k')a\\ &-(k+k')^{-1}\sin(k+k')a].\end{aligned} \quad (I.70)$$

The first term in (I.70) is obtained by a straightforward differentiation of (I.67) with respect to β. The presence of the second term is due to the condition that at $\beta=0$, by definition (I.43), $U_2=0$. The explicit expressions (I.66) and (I.67) do not approach zero as $\beta\rightarrow0+$. Hence they are valid only for $\beta>0$, and at $B=0+$ a step function in β must be added. Taking the derivative of such a step function with respect to β gives rise to a $\delta(\beta)$ function which constitutes the second term in (I.70). At low temperatures, $k\lesssim(\lambda)^{-1}$, the contribution of the second term is $\sim(a/\lambda)^3$.

We notice that as $k\rightarrow\infty$, $\exp(-\beta E)$ varies as $\exp(-2\beta k^2)$. Using (I.69) one sees that, for $\beta>0$, $B\sim k^{-3}\sin ka$ which damps down very rapidly for large k.

For $a=0$, $B=0$ as it should. Expanding B according to powers of a, one obtains $B=B_1+B_2+\cdots$, where

$$\begin{aligned}B_1&=-a\pi^{-2}\delta^3(\mathbf{k}_1+\mathbf{k}_2-\mathbf{k}_1'-\mathbf{k}_2')\exp(-\beta E),\\ B_2&=\pi^{-\frac{5}{2}}a^2\delta^3(\mathbf{k}+\mathbf{k}_2-\mathbf{k}_1'-\mathbf{k}_2')[\exp(-\beta E)]\\ &\times[2kM(\sqrt{2}\beta^{\frac{1}{2}}k)-(2\beta)^{-\frac{1}{2}}\exp(2\beta k^2)].\end{aligned} \quad (I.71)$$

The first order term, B_1, may be put in the form

$$B_1=-V_{12}'\exp(+\beta\nabla_1^2+\beta\nabla_2^2),$$

where

$$V_{12}'=8\pi a\delta^3(\mathbf{r}_1-\mathbf{r}_2).$$

In this form, it is closely related to the pseudopotential[10] discussed in the literature.

The binary kernel in coordinate representation can be obtained from (I.45) and (I.66). It is

$$\begin{aligned}\langle \mathbf{r}_1',\mathbf{r}_2'|B|\mathbf{r}_1,\mathbf{r}_2\rangle &=-2\lambda^{-6}\{\exp[-(\mathbf{r}_1'+\mathbf{r}_2'-\mathbf{r}_1-\mathbf{r}_2)^2/(8\beta)]\}\\ &\times\{a^{-1}\delta(r'-a)\}(1-ar^{-1})\exp[-(r-a)^2/(8\beta)] \quad \text{for } r>a,\\ &=\delta(\beta)[-4\pi rr']^{-1}\delta(r-r')\\ &\times\delta^3[\tfrac{1}{2}(\mathbf{r}_1'+\mathbf{r}_2'-\mathbf{r}_1-\mathbf{r}_2)] \quad \text{for } r\leqq a.\end{aligned} \quad (I.72)$$

where $r=|\mathbf{r}_1-\mathbf{r}_2|$, $r'=|\mathbf{r}_1'-\mathbf{r}_2'|$.

[10] K. Huang and C. N. Yang, Phys. Rev. **105**, 767 (1957); Lee, Huang, and Yang, Phys. Rev. **106**, 1135 (1957).

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APPENDIX A

To prove (I.7) we first observe that a general term in Eq. (I.6) for W_N is a product of m_1 U_1 functions, m_2 U_2 functions, etc., where $\sum lm_l=N$. Such a term gives a contribution

$$\prod_l[l!\Omega b_l(\Omega)]^{m_l}$$

to Q_N. Now in W_N there are, for fixed m_1, m_2, $\cdots$, $N![\prod_l(l!)^{m_l}m_l!]^{-1}$ such terms. Their total contribution to $Q_N(N!)^{-1}$ is thus

$$\prod_l(m_l!)^{-1}[\Omega b_l(\Omega)]^{m_l}.$$

One thus obtains

$$\mathcal{Q}_\Omega=\sum_N z^N \sum_{m_l=0,1,\cdots}' \prod_l \frac{1}{m_l!}[\Omega b_l(\Omega)]^{m_l}$$

$$=\sum_N \sum_{m_l}' \prod_l \frac{1}{m_l!}[\Omega z^l b_l(\Omega)]^{m_l},$$

where the summation, $\sum_{m_l}'$, over m_l is subject to the condition that $\sum lm_l=N$. The subsequent sum $\sum_N$, over N, is equivalent to a removal of this condition on the summation over m_l. Thus

$$\mathcal{Q}_\Omega=\sum_{m_l=0,1,\cdots} \prod_l \frac{1}{m_l!}[\Omega z^l b_l(\Omega)]^{m_l},$$

which leads directly to (I.7).

One may question the mathematical rigor of the above derivation. To make it rigorous we observe that for a fixed Ω,

(a) all Q_N are positive, and

(b) Q_N vanishes for sufficiently large values of N, if the interaction V has a hard repulsive core. $\mathcal{Q}_\Omega$ is thus a polynomial in z with no zeros on the positive real axis. Its logarithm is therefore an analytic function near the origin and all along the positive real axis. Near the origin this logarithm can be expanded as a Taylor's series. It is then easy to see that this Taylor's series is exactly the curly bracket in (I.7). Furthermore, since $\log\mathcal{Q}_\Omega$ is analytic along the positive real axis in the complex z plane, (I.7) is valid for all positive values of z, if one understands the curly bracket to mean the analytic continuation of the power series within.

APPENDIX B

To prove (I.23) and (I.24): The eigenfunctions of H_N can be classified according to the irreducible representations of the permutation group of N objects. If $\psi_i(1',2',\cdots N')$ belongs to an irreducible representation D, then $P'\psi_i(1'\cdots N')$ also belongs to the same representation D. Hence $\sum_{P'} P'\psi_i(1'\cdots N')$ belongs to D. But $\sum_{P'} P'\psi_i(1'\cdots N')$ is symmetrical. Hence if D is not the symmetrical representation, $\sum_{P'} P'\psi_i(1'\cdots N')=0$. On the other hand, if D is the symmetrical representation, then

$$\textstyle\sum_{P'} P'\psi_i(1'\cdots N')=N!\psi_i(1'\cdots N').$$

Using the definitions (I.4) and (I.11), one obtains immediately (I.23). The proof of (I.24) is similar.

Formula (I.23) was first used by Feynman[11] in his treatment of the Bose condensation problem by path integrals.

APPENDIX C

To prove rule A: Each term of the right-hand side of (I.6) is characterized by a grouping of the form (I.27) of the coordinates 1, 2, $\cdots l$. Application of the operation $\sum_{P'}P'$ to both sides of (I.6) therefore naturally leads on the right-hand side to a summation S of the form (I.28), but without the condition stated in the paper for (I.28). The left-hand side is, by (I.23), equal to $\langle 1',\cdots l'|W_l{}^S|1,\cdots l\rangle$. One thus proves that $\langle 1',\cdots l'|W_l{}^S|1,\cdots l\rangle$ is equal to the sum of all S over the different groupings (I.27).

One then substitutes the above result for the left-hand side of (I.12). Solving the resultant equations for $U_1{}^S$, $U_2{}^S$, $U_3{}^S$, $\cdots$ in succession, one obtains rule A by induction.

APPENDIX D

Equation (I.51) is intuitively quite obvious. It is a consequence of the fact that for fixed $\mathbf{r}_1$, integration of U_l over the other $\mathbf{r}$'s gives a result independent of $\mathbf{r}_1$. To fill in the logical steps, we consider the equation $H_N\psi=E\psi$ as an eigenvalue problem in $3N$-dimensional space, within the basic cube

$$\begin{aligned}&\tfrac{1}{2}L\geqq x_i\geqq -\tfrac{1}{2}L, \quad \tfrac{1}{2}L\geqq z_i\geqq -\tfrac{1}{2}L,\\ &\tfrac{1}{2}L\geqq y_i\geqq -\tfrac{1}{2}L, \quad (i=1,2,\cdots N),\end{aligned} \qquad (I.73)$$

with periodic boundary conditions in each of the $3N$ dimensions. An eigenfunction ψ can be continued outside of the cube to all space as a periodic function. Extending the definition of the operator H_N in a periodic way to all space, one has $H_{N\Omega}\psi=E\psi$ *everywhere*. The explicit form of $H_{N\Omega}$ is

$$H_{N\Omega}=-\sum_1^N \nabla_\alpha{}^2+\sum_{\alpha>\beta}\sum_{\mathbf{m}} V(\mathbf{r}_\alpha-\mathbf{r}_\beta+\mathbf{m}L), \quad (I.74)$$

where $\mathbf{m}=(m_x,m_y,m_z)$ has $\pm$ integers as components. [For simplicity we assume here that $V(\mathbf{r})=0$ for $|\mathbf{r}|\geqq r_0$ where r_0=range and is $\ll\frac{1}{2}L$.] Within the basic

[11] R. P. Feynman, Phys. Rev. **91**, 1291 (1953).

cube (I.73), (I.74) is the same as (I.1) except for regions near such edges as, e.g.,

$$x_1=\frac{L}{2},\quad x_2=-\frac{L}{2},\quad y_1=y_2,\quad z_1=z_2.$$

Definition (I.1) *should be amended* to become everywhere identical to (I.74) inside the basic cube. Otherwise the discussion would become more clumsy.

Equation (I.4) can then be regarded as defining $W_{N\Omega}$ for arbitrary values of $\mathbf{r}_1', \cdots \mathbf{r}_N', \mathbf{r}_1, \cdots \mathbf{r}_N$. *It is a function periodic in each of the 6N linear dimensions with a period L.* Furthermore, since the potential energy in (I.74) depends only on the relative coordinates, and not on the coordinates of the center of mass of the N particles, all eigenfunctions can be chosen to be eigenstates of the total momentum so that

$$\psi_\alpha(\mathbf{r}_1+\xi;\mathbf{r}_2+\xi;\cdots\mathbf{r}_N+\xi)=\psi_\alpha(\mathbf{r}_1,\mathbf{r}_2,\cdots\mathbf{r}_N)\exp(i\mathbf{K}_\alpha\cdot\xi).$$

[It is important to realize that the periodicity condition does not invalidate this statement.] One then concludes from (I.4) that

$$\langle\mathbf{r}_1'+\xi,\mathbf{r}_2'+\xi,\cdots|W_{N\Omega}|\mathbf{r}_1+\xi,\mathbf{r}_2+\xi,\cdots\rangle \quad \text{(I.75)}$$

is independent of ξ.

It is clear from the structure of (I.6) that, like $W_{N\Omega}$, $U_{N\Omega}$ also has a $6N$-dimensional periodicity in coordinate space, and also is invariant under a simultaneous displacement of all $2N$ vector coordinates $\mathbf{r}_\alpha'$ and $\mathbf{r}_\alpha$ by the same displacement ξ. From these two properties of $U_{l\Omega}$ it is easy to see that

$$\int\langle\mathbf{r}_1,\mathbf{r}_2,\cdots\mathbf{r}_l|U_{l\Omega}|\mathbf{r}_1,\mathbf{r}_2,\cdots\mathbf{r}_l\rangle d^3r_2d^3r_3,\cdots d^3r_l$$

over the box (I.52) is independent of $\mathbf{r}_1$. Equation (I.51) then follows from (I 10).

APPENDIX E

To establish (I.53) we notice that $W_{l\infty}$, when regarded as a function of β and $\mathbf{r}_1', \mathbf{r}_2', \cdots \mathbf{r}_l'$, with $\mathbf{r}_1, \mathbf{r}_2, \cdots \mathbf{r}_l$ as parameters, satisfies

$$\frac{\partial}{\partial\beta}W_{l\infty}=[-\sum\nabla_\alpha'^2+\sum_{\alpha>\beta}V(\mathbf{r}_\alpha'-\mathbf{r}_\beta')]W_{l\infty}, \quad \text{(I.76)}$$

and

$$W_{l\infty}|_{\beta=0}=\delta^3(\mathbf{r}_1'-\mathbf{r}_1)\delta^3(\mathbf{r}_2'-\mathbf{r}_2)\cdots\delta^3(\mathbf{r}_l'-\mathbf{r}_l). \quad \text{(I.77)}$$

These two equations can also be used to define $W_{l\infty}$. Now we adopt the definition of $W_{l\Omega}$ *over all space* introduced in Appendix D. $W_{l\Omega}$ satisfies

$$\frac{\partial}{\partial\beta}W_{l\Omega}=[-\sum\nabla_\alpha'^2+\sum_{\alpha>\beta}\sum_{\mathbf{m}}V(\mathbf{r}_\alpha'-\mathbf{r}_\beta'+\mathbf{m}L)]W_{l\Omega}, \quad \text{(I.78)}$$

and

$$W_{l\Omega}|_{\beta=0}=[\sum_{\mathbf{m}}\delta^3(\mathbf{r}_1'-\mathbf{r}_1+\mathbf{m}L)]\cdots\times[\sum_{\mathbf{m}}\delta^3(\mathbf{r}_l'-\mathbf{r}_l+\mathbf{m}L)]. \quad \text{(I.79)}$$

These two equations can also be used to define $W_{l\Omega}$.

Equations (I.76) and (I.78) may be regarded as "diffusion equations" (with β=time) while (I.77) and (I.79) serve as the initial conditions. One then sees that $W_{l\infty}$ and $W_{l\Omega}$ differ for two reasons:

(i) The potential energy in (I.78) is different from that in (I.76). The former includes a sum

$$\sum_{\mathbf{m}}V(\mathbf{r}_\alpha'-\mathbf{r}_\beta'+\mathbf{m}L),$$

while the latter contains only the term $\mathbf{m}=0$. However, the terms with $\mathbf{m}\neq 0$ may be regarded as the "images" of this term, and are ineffective except for separations $|\mathbf{r}_\alpha'-\mathbf{r}_\beta'|\gtrsim L$.

(ii) The initial condition (I.79) gives $W_{l\Omega}$ at $\beta=0$ as a sum of many δ^{3l} functions in the $3l$-dimensional space $\mathbf{r}_1', \mathbf{r}_2', \cdots \mathbf{r}_l'$, forming a periodic lattice with period L in each linear dimension. On the other hand, (I.77) gives W_l at $\beta=0$ as a *single* δ^{3l} function.

While diffusion is a process that goes with arbitrary speed, the larger speeds have progressively smaller probability. For finite and fixed values of $\mathbf{r}_1, \mathbf{r}_2, \cdots \mathbf{r}_l$ (which determine the positions of the δ^{3l} functions in the initial conditions), and at a fixed β and fixed $\mathbf{r}_1', \mathbf{r}_2', \cdots \mathbf{r}_l'$, the two differences between $W_{l\Omega}$ and $W_{l\infty}$ described above become unimportant as $L\rightarrow\infty$. Therefore $W_{l\Omega}\rightarrow W_{l\infty}$. By (I.23) and (I.24), the same holds for $W_{l\Omega}^S$ and $W_{l\Omega}^A$. From (I.6) and (I.12) one easily proves that also $U_{l\Omega}\rightarrow U_{l\infty}$, $U_{l\Omega}^S\rightarrow U_{l\infty}^S$, and $U_{l\Omega}^A\rightarrow U_{l\infty}^A$.

In fact, for a given potential V it is possible to evaluate the difference between $W_{l\Omega}$ and $W_{l\infty}$ in terms of B_∞. We shall illustrate such a computation for the case of hard sphere interactions.

For simplicity let us first consider the case $l=2$. In this case, B_∞ and $U_{2\infty}$ (consequently, also $W_{2\infty}$) are given explicitly by (I.72) and (I.66). To express $W_{2\Omega}$ and $U_{2\Omega}$ in terms of these functions, we introduce a W_2' function which satisfies the differential equation

$$\frac{\partial}{\partial\beta}W_2'=\left[-\sum_{\alpha=1}^{2}\nabla_\alpha'^2+\sum_{\mathbf{m}}V(\mathbf{r}_1'-\mathbf{r}_2'+\mathbf{m}L)\right]W_2', \quad \text{(I.80)}$$

but with the initial condition

$$W_2'|_{\beta=0}=\delta^3(\mathbf{r}_1'-\mathbf{r}_1)\delta^3(\mathbf{r}_2'-\mathbf{r}_2). \quad \text{(I.81)}$$

It is easy to see that $W_{2\Omega}$ is related to W_2' by

$$\langle\mathbf{r}_1',\mathbf{r}_2'|W_{2\Omega}|\mathbf{r}_1,\mathbf{r}_2\rangle=\sum_{\mathbf{m}_1,\mathbf{m}_2}\langle\mathbf{r}_1'+\mathbf{m}_1L,\mathbf{r}_2'+\mathbf{m}_2L|W_2'|\mathbf{r}_1,\mathbf{r}_2\rangle. \quad \text{(I.82)}$$

Although W_2' satisfies a different "differential equation" from $W_{2\infty}$, they both satisfy the same initial condition. By going through a series of arguments similar to those used in Sec. 4, we can express W_2' in terms of $W_{2\infty}$ and B_∞:

$$\begin{aligned}
\langle \mathbf{r}_1',\mathbf{r}_2'|W_2'|\mathbf{r}_1,\mathbf{r}_2\rangle &= \langle \mathbf{r}_1',\mathbf{r}_2'|W_{2\infty}|\mathbf{r}_1,\mathbf{r}_2\rangle \\
&+\sum_{\mathbf{m}\neq 0}\langle \mathbf{r}_1'-\mathbf{m}L,\,\mathbf{r}_2'|U_{2\infty}|\mathbf{r}_1-\mathbf{m}L,\,\mathbf{r}_2\rangle \\
&+\sum_{\mathbf{m}\neq\mathbf{m}'}\sum_{\mathbf{m}'}\int_0^\beta d\beta'\int d^3\mathbf{r}_1''d^3\mathbf{r}_2'' \\
&\times\langle \mathbf{r}_1'-\mathbf{m}L,\,\mathbf{r}_2'|U_{2\infty}(\beta-\beta')|\mathbf{r}_1''-\mathbf{m}L,\,\mathbf{r}_2''\rangle \\
&\times\langle \mathbf{r}_1''-\mathbf{m}'L,\,\mathbf{r}_2''|B_\infty(\beta')|\mathbf{r}_1-\mathbf{m}'L,\,\mathbf{r}_2\rangle \\
&+\sum_{m\neq m'}\sum_{m'\neq m''}\sum_{m''}\int_0^\beta d\beta'\int_0^{\beta'} d\beta''\int d^3r_1''d^3r_2''d^3r_1''' \\
&\times d^3r_2'''\langle \mathbf{r}_1'-\mathbf{m}L,\,\mathbf{r}_2'|U_{2\infty}(\beta-\beta')|\mathbf{r}_1''-\mathbf{m}L,\,\mathbf{r}_2''\rangle \\
&\times\langle \mathbf{r}_1''-\mathbf{m}'L,\,\mathbf{r}_2''|B_\infty(\beta'-\beta'')|\mathbf{r}_1'''-\mathbf{m}'L,\,\mathbf{r}_2'''\rangle \\
&\times\langle \mathbf{r}_1'''-\mathbf{m}''L,\,\mathbf{r}_2'''|B_\infty(\beta'')|\mathbf{r}_1-\mathbf{m}''L,\,\mathbf{r}_2\rangle+\cdots.
\end{aligned} \tag{I.83}$$

Equations (I.82) and (I.83) express precisely the physical effects discussed in (i) and (ii) above. Together these two equations give the explicit form of $W_{2\Omega}$ in terms of the binary function B_∞.

By using (I.72) and (I.66) it can be shown that for fixed positions of $\mathbf{r}_1$, $\mathbf{r}_2$ and $\mathbf{r}_1'$, $\mathbf{r}_2'$ as $L\rightarrow\infty$, (I.82) becomes

$$W_{2\Omega}=W_2'+O[\exp(-L^2/4\beta)], \tag{I.84}$$

and (I.83) becomes

$$W_2'=W_{2\Omega}+O[\exp(-L^2/2\beta)]. \tag{I.85}$$

Thus we have

$$W_{2\Omega}\rightarrow W_{2\infty}\quad\text{as}\quad \Omega\rightarrow\infty. \tag{I.86}$$

By using (I.82) and (I.83) we can also express $b_2(\Omega)$ explicitly in terms of B_∞. It is easy to see that $\lim_{\Omega\rightarrow\infty}b_2(\Omega)$ is given by (I.53).

We remark that

$$W_{2\Omega}=W_{2\infty}+O[\exp(-L^2/4\beta)] \tag{I.87}$$

is due to the familiar property of diffusion equations: i.e., the probability for a particle to travel a distance L in a time "β" is proportional to $\exp[-L^2/(4\beta)]$. Consequently, (I.87) is not limited to the case of hard spheres. It is valid for any potential with a finite range.

In an entirely similar manner one can express the difference between $W_{l\Omega}$ and $W_{l\infty}$ in terms of B_∞ and show explicitly that (I.53) is correct for any $l\geqq 2$. The main points in the proof are the following two facts. First, the integrand in (I.51) approaches that in (I.53) as $L\rightarrow\infty$. Second, in the region of integration defined by (I.52), the integrand in (I.51) is peaked at the center. It becomes exponentially small far away from the center, as can be seen by arguments similar to the above arguments for the case $l=2$. The limit as $\Omega\rightarrow\infty$ of the integral (I.51) is thus equal to the integral of the limit of the integrand over all space.