

Multiple Scattering and Many-Body Theory: Free Energy of Electrons in Helium

M. COOPERSMITH*

Department of Physics and Institute for the Study of Metals,† University of Chicago, Chicago, Illinois
and

Physics Department, Case Institute of Technology, Cleveland, Ohio

(Received 12 April 1965)

An electron in helium vapor at 4°K is characterized by its *s*-wave scattering length off helium atoms. This scattering length is small compared with the average interparticle spacing in the helium vapor. Consequently, we have taken as a model a particle interacting via hard-core repulsion with an ideal gas. This establishes a connection with the hard-sphere Bose problem of more general interest. The model described above is simpler (a) because it has only Boltzmann statistics and (b) because the electron is very light compared with the helium atoms. For this model, we have calculated the interaction free energy of the electron assuming that it is in statistical equilibrium with the helium gas. In the *s*-wave approximation, it is shown that this interaction free energy is rigorously $2\pi\rho a(\hbar^2/m)$ due to single scattering, all higher order multiple-scattering effects being zero. Here, ρ is the average density of helium atoms, a is the scattering length, and m is the electron mass. Since the *p*-wave approximation contributes a term of order ρa^3 , it is evident that the term $2\pi\rho a(\hbar^2/m)$ is good to higher densities than might previously have been supposed. This provides partial justification for the "bubble" model of the electron mobility since the term $2\pi\rho a(\hbar^2/m)$ is certainly good up to densities at which the free energy of the "bubble" configuration becomes smaller.

I. INTRODUCTION

THE anomalous behavior of electron mobility in helium vapor at about 4°K has been studied both theoretically and experimentally by a number of people.¹ The anomaly can be simply stated for the present purpose as an enormous decrease (a factor of approximately 10^3) in the free-electron mobility for pressures greater than some critical pressure which is near the saturated vapor pressure. The problem we wish to consider is the formulation of a statistical-mechanical theory of electrons in helium vapor at low temperatures. Leaving aside the question of a macroscopic model (which has already been disposed of²), we shall adopt the following simple (and perhaps simplest) microscopic model and try to deduce the equilibrium and non-equilibrium properties of this system. The nonequilibrium property of interest, namely the mobility, will turn out for the present to represent a far more difficult calculation than the equilibrium properties, but we shall see that the equilibrium properties alone will give us some insight as to why the macroscopic (bubble) model works.

II. FORMULATION

Since the bubble model involves only one microscopic experimentally measured parameter, namely, the low-energy scattering length of electrons off helium atoms, we adopt a Hamiltonian in which the electron-helium interaction is characterized by just this length. For the practical purposes of calculation, we shall regard this interaction as a hard-core repulsion with the radius of the hard core equal to the scattering length. Such an

interaction is consistent with the pseudopotential for electron scattering off helium atoms.³ At present, we shall regard the helium system as simply an ideal gas, which it indeed approximates at the densities under consideration. The Hamiltonian for one electron in a helium gas is thus

$$H = T_{\text{He}} + T_e + \sum_{i=1}^N V(|\mathbf{r}_i - \mathbf{r}_e|), \quad (1)$$

where T_{He} and T_e are the helium and electron kinetic energies, respectively, and $V(|\mathbf{r}_i - \mathbf{r}_e|) [\equiv V(r_{ie})]$ is the interaction potential between the electron and the *i*th helium atom. V in this case is the hard-core potential described above so that

$$\begin{aligned} V(r) &= \infty, & r < a, \\ V(r) &= 0, & r > a. \end{aligned} \quad (2)$$

We now wish to calculate the interaction free energy of the electron with the helium system. We may think of an ensemble of systems containing one electron each in which the helium atoms are allowed to have all possible configurations consistent with the interaction. This defines a canonical ensemble in which the (Helmholz) free energy is given by

$$\begin{aligned} -\beta F &= \ln \text{tr} e^{-\beta H}, \\ &= \ln \text{tr} \exp \left[-\beta \left(\sum_{i=1}^N \frac{\hbar^2 k_i^2}{2M} + \frac{\hbar^2 k^2}{2m} + \sum_{i=1}^N V(r_{ie}) \right) \right]. \end{aligned} \quad (3)$$

Here M is the helium mass and m is the electron mass. Since $M \gg m$, we can treat the electron-helium center of mass as the center of mass of the helium cluster. (This statement will become more precise later in the calculation.) We can thus commute the entire helium kinetic energy with the rest of the Hamiltonian and we

* Present address: Physics Department, Case Institute of Technology, Cleveland, Ohio.

† Work supported by the National Science Foundation.

¹ See, for example, J. Levine and T. M. Sanders, Phys. Rev. Letters 8, 159 (1962) and references quoted therein.

² See Ref. 1.

³ J. Jortner (private communication).

get

$$\begin{aligned}
 -\beta F &= \log \operatorname{tr} \exp \left(-\beta \sum_{i=1}^N \frac{\hbar^2 k_i^2}{2M} \right) \\
 &\quad + \log \operatorname{tr} \exp \left[-\beta \left(\frac{\hbar^2 k^2}{2m} + \sum_{e=1}^N V(r_{ie}) \right) \right], \\
 &= -\beta F_{\text{He}} - \beta F_I. \tag{4}
 \end{aligned}$$

The helium system acts simply as a classical ideal gas.

The mass which occurs in the interaction free energy should, of course, be a kind of reduced mass but for practical purposes it is equal to the electron mass. The above approximation is equivalent to the adiabatic approximation since the helium atoms are taken to be stationary scattering centers for the electron in F_I . They are, of course, allowed to move as a classical fluid.

The quantity of interest being F_I , we resort to the usual⁴ cluster expansion. F_I is first rewritten as follows:

$$\begin{aligned}
 -\beta F_I &= \ln \operatorname{tr} \exp \left[-\left(\frac{\lambda^2 k^2}{2} + \beta \sum_{i=e}^N V(r_{ie}) \right) \right], \\
 &= \ln \operatorname{tr} \exp \left(-\frac{\lambda^2 k^2}{2} \right) + \ln \left\{ \operatorname{tr} \exp \left[-\left(\lambda^2 k^2 / 2 + \beta \sum_{i=e}^N V(r_{ie}) \right) \right] / \operatorname{tr} \exp \left(-\lambda^2 k^2 / 2 \right) \right\}, \\
 &= -\beta F_e - \beta \Delta F, \tag{5}
 \end{aligned}$$

where $\lambda = (\hbar^2 \beta / m)^{1/2}$ is proportional to the thermal wavelength of the electron. For the rest of the computation, we work with the quantity ΔF . We have

$$\begin{aligned}
 -\beta \Delta F &= \ln \left[\operatorname{tr} \exp \left(-\frac{\lambda^2 k^2}{2} \right) \exp \left(-\sum_{i=1}^N \int_0^\beta V_i(\beta) d\beta \right) \right] / \operatorname{tr} \exp \left(-\frac{\lambda^2 k^2}{2} \right), \\
 &= \ln \left\langle \exp \left(-\sum_{i=1}^N \int_0^\beta V_i(\beta) d\beta \right) \right\rangle, \\
 &= \ln \left\langle \prod_{i=1}^N g_i(\beta) \right\rangle, \\
 &= \ln \left\langle \prod_{i=1}^N (1 + f_i(\beta)) \right\rangle, \\
 &= \sum_{i=1}^N \langle f_i(\beta) \rangle + \sum_{i < j=1}^N [\langle f_i f_j \rangle - \langle f_i \rangle \langle f_j \rangle] + \dots \tag{6}
 \end{aligned}$$

$V_i(\beta)$ is the interaction representation of $V(r_{ie})$, while g_i is its exponential, the product is ordered to give the exponential of the sum, and angular brackets mean average. The last term is a sum of semi-invariants of which we have exhibited the first two.

At first sight, it appears that we have accomplished little, if anything, by all this rearranging and expanding. Indeed, if we were dealing with a purely classical system, the only term to survive would be the first since the rest are all unlinked by translational invariance. Since, in the quantum-mechanical case, all terms are coupled, the expansion looks like some kind of virial series, but as we shall see, the second term is infinite at zero temperature and we are thus forced to "sum to infinite order" which in this case appears to be the entire series.

III. MULTIPLE-SCATTERING THEORY

To see immediately that the last statement represents an impossibility, we need only notice that summing the entire series implies evaluating the n th term and this, of course, means solving the problem of a Hamiltonian with n spherically symmetric interaction terms. In fact, if we had been able to solve this, we would

not have had to make the expansion at all since the solution for $n=N$ would give us all the energy levels directly. But it is just this fact which enables us to find an approximation scheme for this problem. First, we do some more rewriting:

$$-\beta \Delta F = \sum_{i=1}^N \langle g_i - 1 \rangle + \sum_{i < j=1}^N [\langle g_i g_j \rangle - \langle g_i \rangle \langle g_j \rangle] + \dots, \tag{7}$$

where we have noticed that g 's can be substituted for f 's in all semi-invariants but the first. Now, the products of g 's in the averages are ordered. This means, for example, that

$$\begin{aligned}
 g_i g_j &= \exp \left[-\left(\lambda^2 k^2 / 2 + \beta V(r_{ie}) + \beta V(r_{je}) \right) \right], \\
 &= \exp(-\beta H^{(ij)}), \tag{8}
 \end{aligned}$$

where $H^{(i,j)}$ stands for the Hamiltonian of an electron with two scattering centers. Since the average of the ordered product of g 's involves a trace, we must find wave functions for an electron with n spherically symmetric scattering centers as stated. In the present context we "simply" have to find a wave function which satisfies the free-particle Schrödinger equation and the

⁴ R. Kubo, J. Phys. Soc. Japan 17, 1100 (1962).

boundary condition of being zero on n spheres of radius a , the scattering length. Let us first do this for the trivial case of one scattering center. Since we are interested in a trace, we are free to choose any representation we please. For mathematical convenience and physical interest, we use the coordinate representation and write the wave function as a plane wave plus a scattered wave. This amounts to picking a particular linear combination of radial wave functions and spherical harmonics. We pick a wave function which obviously satisfies the wave equation and require that it go to zero on a sphere of radius a . Since we are dealing with very low energy (the Gaussian in the trace limits k values to essentially less than $1/\lambda$), we have $ka < a/\lambda \sim 1/200 \ll 1$ at 4°K so that we need concern ourselves only with spherically symmetric scattered waves.

$$\Psi_{(1)}(\mathbf{r}_{ei}) = e^{i\mathbf{k}\cdot\mathbf{r}_{ei}} + A_1(e^{i\mathbf{k}r_{ei}}/kr_{ei}) \quad (9)$$

using δ -function normalization. Expanding the plane wave in spherical harmonics and setting the wave function equal to zero at $r_{e1} = a$, we have

$$\sin ka/ka + A_1(e^{ika}/ka) = 0, \quad (10)$$

or

$$A_1 = -\sin ka/e^{ika} = (e^{-2ika} - 1)/2i, \quad (11)$$

which is the usual result for s -wave scattering from a hard sphere. We now try the same trick for n scattering centers, namely, we write the wave function as⁵

$$\Psi_{(n)}(\{\mathbf{r}_{ei}\}) = e^{i\mathbf{k}\cdot\mathbf{r}_{e1}} + A_1 \frac{e^{i\mathbf{k}r_{e1}}}{kr_{e1}} + A_2 \frac{e^{i\mathbf{k}r_{e2}}}{kr_{e2}} + \dots + A_n \frac{e^{i\mathbf{k}r_{en}}}{kr_{en}}. \quad (12)$$

This function clearly satisfies the free-particle wave equation. To determine the coefficients A_i , we expand all terms but the i th around the i th center and equate the wave function to zero at $r_{ei} = a$, keeping only s -wave parts. The result of all this is the following system of n linear equations:

$$\begin{aligned} \frac{\sin ka}{ka} + A_1 \frac{e^{ika}}{ka} + A_2 \frac{e^{i\mathbf{k}r_{12}} \sin ka}{k^2 r_{12} a} + \dots + A_n \frac{e^{i\mathbf{k}r_{1n}} \sin ka}{k^2 r_{1n} a} &= 0, \\ \frac{e^{i\mathbf{k}\cdot\mathbf{r}_{12}} \sin ka}{ka} + A_1 \frac{e^{i\mathbf{k}r_{21}} \sin ka}{k^2 r_{21} a} + A_2 \frac{e^{ika}}{ka} + \dots + A_n \frac{e^{i\mathbf{k}r_{2n}} \sin ka}{k^2 r_{2n} a} &= 0, \\ \vdots \\ \frac{e^{i\mathbf{k}\cdot\mathbf{r}_{1n}} \sin ka}{ka} + A_1 \frac{e^{i\mathbf{k}r_{n1}} \sin ka}{k^2 r_{n1} a} + A_2 \frac{e^{i\mathbf{k}r_{n2}} \sin ka}{k^2 r_{n2} a} + \dots + A_n \frac{e^{ika}}{ka} &= 0, \end{aligned} \quad (13)$$

⁵ This form of the wave function is similar to that used by L. Foldy in the treatment of multiple scattering of waves. See L. Foldy, Phys. Rev. 67, 107 (1945). The spirit of the present calculation is somewhat different, however.

the solution of which we write in determinantal form as

$$A_i = \frac{-\sin ka \begin{vmatrix} 1 & e^{ika} & \dots & \frac{e^{i\mathbf{k}r_{1n}} \sin ka}{kr_{1n}} \\ e^{i\mathbf{k}\cdot\mathbf{r}_{12}} & \frac{e^{i\mathbf{k}r_{21}} \sin ka}{kr_{21}} & \dots & \frac{e^{i\mathbf{k}r_{2n}} \sin ka}{kr_{2n}} \\ \vdots & \vdots & \ddots & \vdots \\ e^{i\mathbf{k}\cdot\mathbf{r}_{1n}} & \frac{e^{i\mathbf{k}r_{n1}} \sin ka}{kr_{n1}} & \dots & e^{ika} \end{vmatrix}}{\begin{vmatrix} e^{ika} & \frac{e^{i\mathbf{k}r_{12}} \sin ka}{kr_{12}} & \dots & \frac{e^{i\mathbf{k}r_{1n}} \sin ka}{kr_{1n}} \\ \frac{e^{i\mathbf{k}r_{21}} \sin ka}{kr_{21}} & e^{ika} & \dots & \frac{e^{i\mathbf{k}r_{2n}} \sin ka}{kr_{2n}} \\ \vdots & \vdots & \ddots & \vdots \\ \frac{e^{i\mathbf{k}r_{n1}} \sin ka}{kr_{n1}} & \frac{e^{i\mathbf{k}r_{n2}} \sin ka}{kr_{n2}} & \dots & e^{ika} \end{vmatrix}}, \quad (14)$$

where we have multiplied Eq. (13) by ka . This determines the wave function [Eq. (12)]. Two remarks must now be made regarding this wave function. The first has to do with the approximation of expanding all terms and keeping only s -wave parts. For the single-scattering problem, we know that this satisfies the boundary condition to order $(ka)^3$ since this is the p -wave part of the plane wave. For the multiple-scattering case, the approximation clearly depends on the separation between scattering centers since we are expanding spherical waves from one origin about another origin. The p -wave terms from the spherical waves are of order $(a/r_{ij})^3$ where r_{ij} is the distance between the i th and j th scattering centers. For most distributions in the canonical ensemble, r_{ij} will be of the order of the mean interparticle spacing so that the p -wave term will be of order ρa^3 , where ρ is the mean density. For the present case of helium vapor at about one atmosphere pressure and 4°K, we have $\rho a^3 \sim 1/300$ so the p -wave term may be dispensed with.

The second remark concerns the question of normalization of the multiple-scattered wave function. For the single-scattering problem, the integral of $\Psi^* \Psi$ over a box of volume Ω goes like $\Omega \cdot v_c$ where v_c is the hard-core "excluded" volume, $\frac{4}{3}\pi a^3$. For multiple scattering from n scattering centers distributed throughout a finite volume, it is a straightforward matter to convince oneself that the normalization will go like $\Omega \cdot n v_c$ provided one makes the assumption that the normalization is independent of volume shape for large volumes. In fact, the very condition on the coefficients A_i which makes the wave function zero on the boundaries of the hard spheres eliminates all cross products of spherical waves in the normalization. The excluded volume of the

hard spheres does not affect the value of the trace as long as n/Ω is much smaller than ρ . Unfortunately, a rigorous basis for the above statements is directly tied up with the fundamental question of interchangeability of limits in many-body theory, so that for the present, one must proceed with the pious hope that the end will justify the means.

IV. COMBINATORICS AND INTEGRATION (PRELIMINARIES)

We now show how to use the multiple-scattered wave function obtained in Sec. II to calculate ΔF . The approximation scheme will become clear during the course of the calculation. We start with the first term in the expansion of $-\beta\Delta F$, namely $\sum_{i=1}^N \langle g_i - 1 \rangle$.

$$\begin{aligned}
 \sum_{i=1}^N \langle g_i - 1 \rangle &= N \langle g_1 - 1 \rangle \\
 &= N \left(\frac{\text{tr} \exp[-(\lambda^2 k^2/2 + \beta V)]}{\text{tr} \exp(-\lambda^2 k^2/2)} - 1 \right) \\
 &= N \left[\frac{\int \int \langle r_e | e^{-\beta H^{(1)}} | r_e \rangle d\mathbf{r}_e d\mathbf{r}_1}{\int \int \langle r_e | \exp\left(-\frac{\lambda^2 k^2}{2}\right) | r_e \rangle d\mathbf{r}_e d\mathbf{r}_1} - 1 \right] \\
 &= N \left[\frac{\int \int \int \Psi_{(1)k}^*(r_{e1}) \Psi_{(1)k}(r_{e1}) \exp\left(-\frac{k^2 \lambda^2}{2}\right) d\mathbf{k} d\mathbf{r}_e d\mathbf{r}_1}{\int \int e^{-i\mathbf{k} \cdot \mathbf{r}_{e1}} e^{i\mathbf{k} \cdot \mathbf{r}_{e1}} \exp\left(-\frac{\lambda^2 k^2}{2}\right) d\mathbf{k} d\mathbf{r}_e d\mathbf{r}_1} - 1 \right] \\
 &= N \left[\frac{\int \int \int \left(e^{-i\mathbf{k} \cdot \mathbf{r}_{e1}} - \frac{\sin ka}{e^{-ika}} \frac{e^{-ikr_{e1}}}{kr_{e1}} \right) \left(e^{i\mathbf{k} \cdot \mathbf{r}_{e1}} - \frac{\sin ka}{e^{ika}} \frac{e^{ikr_{e1}}}{kr_{e1}} \right) \exp\left(-\frac{\lambda^2 k^2}{2}\right) d\mathbf{k} d\mathbf{r}_e d\mathbf{r}_1}{(2\pi)^{3/2} \Omega^2} - 1 \right]. \quad (15)
 \end{aligned}$$

Since the Gaussian limits the values of k to less than $1/\lambda$, we expand everything in powers of ka in Eq. (15). This gives us

$$\begin{aligned}
 \sum_{i=1}^N \langle g_i - 1 \rangle &= N \left[\frac{\int \int \int \left[e^{-i\mathbf{k} \cdot \mathbf{r}_{e1}} - \left(\frac{a}{r_{e1}} + \frac{ika^2}{r_{e1}} + \dots \right) e^{-ikr_{e1}} \right] \left[e^{i\mathbf{k} \cdot \mathbf{r}_{e1}} - \frac{a}{r_{e1}} - \frac{ika^2}{r_{e1}} e^{ikr_{e1}} \right] \exp\left(-\frac{\lambda^2 k^2}{2}\right) d\mathbf{k} d\mathbf{r}_e d\mathbf{r}_1 - 1}{((2\pi)^{3/2}/\lambda^3)\Omega^2} \right] \\
 &= N \frac{4\pi \int_0^\infty \int_0^\infty \left[-\frac{ak}{r_{e1}^2} \sin kr_{e1} (e^{ikr_{e1}} + e^{-ikr_{e1}}) \exp\left(-\frac{\lambda^2 k^2}{2}\right) \right] d\mathbf{k} d\mathbf{r}_{e1}}{((2\pi)/\lambda^3)^{3/2} \Omega} \\
 &= N \frac{4\pi \lambda^3 \int_0^\infty \int_0^\infty \frac{ak}{r_{e1}^2} \sin 2kr_{e1} \exp\left(-\frac{\lambda^2 k^2}{2}\right) d\mathbf{k} d\mathbf{r}_{e1}}{(2\pi)^{3/2} \Omega} \\
 &= N \left[4\pi \lambda^3 \int \frac{a}{r_{e1}^2} \frac{\partial}{\partial 2r_{e1}} \int_0^\infty \cos 2kr_{e1} \exp\left(-\frac{\lambda^2 k^2}{2}\right) d\mathbf{k} d\mathbf{r}_{e1} \right] / (2\pi)^{3/2} \Omega \\
 &= 4\pi \rho a \lambda^3 \left[\frac{(2\pi)^{1/2}}{2\lambda r_{e1}^2} \frac{\partial}{\partial 2r_{e1}} e^{-2r_{e1}^2/\lambda^2} d\mathbf{r}_{e1} / (2\pi)^{3/2} \right] \\
 &= -4\pi \rho a \left[(2\pi)^{1/2} \times 4\pi \int_0^\infty r_{e1} e^{-2r_{e1}^2/\lambda^2} dr_{e1} / (2\pi)^{3/2} \right] \\
 &= -2\pi \rho a \lambda^2 \quad (16)
 \end{aligned}$$

to first order in the scattering length. It is important to note that this is not the first-order term itself but the "first order" of the first term, so to speak. What we shall now do is find the first order of all the higher order terms. We first note that the order of magnitude of succeeding orders in the first term goes down like a/λ which is exceedingly small, a very desirable expansion parameter indeed. We therefore expand all terms in powers of ka and try to evaluate the terms with lowest power of a for a given power of the density. The second term will make this clear. From the evaluation of the first term [Eq. (15)], we see that the relevant quantity is $\Psi_{(n)}^* \Psi_{(n)}$. We write it out in full detail for $n=2$:

$$\begin{aligned} & \Psi_{(2)}^* (\{\mathbf{r}_{ei}\}) \Psi_{(2)} (\{\mathbf{r}_{ei}\}) \\ &= 1 - a \left[\frac{e^{ikr_{e1}}}{r_{e1}} e^{-ik \cdot \mathbf{r}_{e1}} + \frac{e^{-ikr_{e1}}}{r_{e1}} e^{ik \cdot \mathbf{r}_{e1}} + \frac{e^{ikr_{e2}}}{r_{e2}} e^{-ik \cdot \mathbf{r}_{e2}} + \frac{e^{-ikr_{e2}}}{r_{e2}} e^{ik \cdot \mathbf{r}_{e2}} \right] \\ & \quad + a^2 \left[\frac{1}{r_{12} r_{e1}} (e^{ikr_{12}} e^{-ik \cdot \mathbf{r}_{e2}} e^{ikr_{e1}} + e^{-ikr_{12}} e^{ik \cdot \mathbf{r}_{e2}} e^{-ikr_{e1}}) + \frac{1}{r_{12} r_{e2}} (e^{ikr_{12}} e^{-ik \cdot \mathbf{r}_{e1}} e^{ikr_{e2}} + e^{-ikr_{12}} e^{ik \cdot \mathbf{r}_{e1}} e^{-ikr_{e2}}) \right. \\ & \quad + \frac{ik}{r_{e1}} (e^{ikr_{e1}} e^{-ik \cdot \mathbf{r}_{e1}} - e^{-ikr_{e1}} e^{ik \cdot \mathbf{r}_{e1}}) + \frac{ik}{r_{e2}} (e^{ikr_{e2}} e^{-ik \cdot \mathbf{r}_{e2}} - e^{-ikr_{e2}} e^{ik \cdot \mathbf{r}_{e2}}) \\ & \quad \left. + \frac{1}{r_{e1}^2} + \frac{1}{r_{e2}^2} + \frac{1}{r_{e1} r_{e2}} (e^{ikr_{e1}} e^{-ik \cdot \mathbf{r}_{12}} e^{-ikr_{e2}} + e^{-ikr_{e1}} e^{ik \cdot \mathbf{r}_{12}} e^{ikr_{e2}}) \right] \\ & \quad + a^3 \left[\frac{2k^2}{3r_{e1}} (e^{ikr_{12}} e^{-ik \cdot \mathbf{r}_{12}} + e^{-ikr_{12}} e^{ik \cdot \mathbf{r}_{12}}) + \frac{2k^2}{3r_{e2}} (e^{ikr_{e2}} e^{-ik \cdot \mathbf{r}_{e2}} + e^{-ikr_{e2}} e^{ik \cdot \mathbf{r}_{e2}}) \right. \\ & \quad + \frac{2ik}{r_{12} r_{e1}} (e^{-ikr_{12}} e^{-ikr_{e1}} e^{ik \cdot \mathbf{r}_{e2}} - e^{ikr_{12}} e^{ikr_{e1}} e^{-ik \cdot \mathbf{r}_{e2}}) + \frac{2ik}{r_{12} r_{e2}} (e^{-ikr_{12}} e^{-ikr_{e2}} e^{ik \cdot \mathbf{r}_{e1}} - e^{ikr_{12}} e^{ikr_{e2}} e^{-ik \cdot \mathbf{r}_{e1}}) \\ & \quad - \frac{1}{r_{12} r_{e1}^2} (e^{ik \cdot \mathbf{r}_{12}} e^{ikr_{12}} + e^{-ik \cdot \mathbf{r}_{12}} e^{-ikr_{12}}) - \frac{1}{r_{12} r_{e2}^2} (e^{ik \cdot \mathbf{r}_{12}} e^{-ikr_{12}} + e^{-ik \cdot \mathbf{r}_{12}} e^{ikr_{12}}) \\ & \quad \left. - \frac{1}{r_{12} r_{e1} r_{e2}} (e^{ikr_{12}} e^{ikr_{e1}} e^{-ikr_{e2}} + e^{-ikr_{12}} e^{-ikr_{e1}} e^{ikr_{e2}} + e^{ikr_{12}} e^{-ikr_{e1}} e^{ikr_{e2}} + e^{-ikr_{12}} e^{ikr_{e1}} e^{-ikr_{e2}}) \right] + \dots, \quad (17) \end{aligned}$$

where we have stopped at the a^3 term since the next higher power is contributed to by p -wave scattering. In order to see what is going on, we calculate the diagonal matrix elements of $e^{-\beta H^{(2)}}$ using Eq. (17).

$$\begin{aligned} & \langle \mathbf{r}_e | e^{-\beta H^{(2)}} | \mathbf{r}_e \rangle \\ &= \int \Psi_{(2)}^* \Psi_{(2)} \exp\left(-\frac{\lambda^2 k^2}{2}\right) d\mathbf{k}, \\ &= \frac{(2\pi)^{3/2}}{\lambda^3} - 4\pi a \int_0^\infty \left[\frac{k \sin 2kr_{e1}}{r_{e1}^2} + \frac{k \sin 2kr_{e2}}{r_{e2}^2} \right] \exp\left(-\frac{\lambda^2 k^2}{2}\right) dk \\ & \quad + 4\pi a^2 \int_0^\infty \left[\frac{2k \sin k(r_{e1} + r_{12} + r_{e2})}{r_{e1} r_{12} r_{e2}} + \frac{k^2 \cos 2kr_{e1}}{r_{e1}^2} + \frac{k^2 \cos 2kr_{e2}}{r_{e2}^2} \right] \exp\left(-\frac{\lambda^2 k^2}{2}\right) dk \\ & \quad + 4\pi a^3 \int_0^\infty \left[\frac{2k^3 \sin 2kr_{e1}}{3r_{e1}^2} + \frac{2k^3 \sin 2kr_{e2}}{3r_{e2}^2} - \frac{k^2 \cos k(r_{e1} + r_{12} + r_{e2})}{4r_{e1} r_{12} r_{e2}} \right. \\ & \quad \left. - \frac{k \sin k(2r_{e1} + 2r_{12})}{r_{e1}^2 r_{12}^2} - \frac{k \sin k(2r_{e2} + 2r_{12})}{r_{e2}^2 r_{12}^2} \right] \exp\left(-\frac{\lambda^2 k^2}{2}\right) dk, \end{aligned}$$

$$\begin{aligned}
 &= \frac{(2\pi)^{2/3}}{\lambda^3} + 4\pi a \left[\frac{1}{r_{e1}^2} \frac{\partial}{\partial(2r_{e1})} \int_0^\infty \cos 2kr_{e1} \exp\left(-\frac{\lambda^2 k^2}{2}\right) dk + \frac{1}{r_{e2}^2} \frac{\partial}{\partial(2r_{e2})} \int_0^\infty \cos 2kr_{e2} \exp\left(-\frac{\lambda^2 k^2}{2}\right) dk \right] \\
 &\quad - 4\pi a^2 \left[\frac{2}{r_{e1}r_{12}r_{e2}} \frac{\partial}{\partial(r_{e1}+r_{12}+r_{e2})} \int_0^\infty \cos k(r_{e1}+r_{12}+r_{e2}) \exp\left(-\frac{\lambda^2 k^2}{2}\right) dk \right. \\
 &\quad \left. + \frac{1}{r_{e1}^2} \frac{\partial^2}{\partial(2r_{e1})^2} \int_0^\infty \cos 2kr_{e1} \exp\left(-\frac{\lambda^2 k^2}{2}\right) dk + \frac{1}{r_{e2}^2} \frac{\partial^2}{\partial(2r_{e2})^2} \int_0^\infty \cos 2kr_{e2} \exp\left(-\frac{\lambda^2 k^2}{2}\right) dk \right] \\
 &\quad + 4\pi a^3 \left[\frac{2}{3r_{e1}^2} \frac{\partial^3}{\partial(2r_{e1})^3} \int_0^\infty \cos 2kr_{e1} \exp\left(-\frac{\lambda^2 k^2}{2}\right) dk + \frac{2}{3r_{e2}^2} \frac{\partial^3}{\partial(2r_{e2})^3} \int_0^\infty \cos 2kr_{e2} \exp\left(-\frac{\lambda^2 k^2}{2}\right) dk \right. \\
 &\quad \left. + \frac{4}{r_{e1}r_{12}r_{e2}} \frac{\partial^2}{\partial(r_{e1}+r_{12}+r_{e2})^2} \int_0^\infty \cos k(r_{e1}+r_{12}+r_{e2}) \exp\left(-\frac{\lambda^2 k^2}{2}\right) dk + \frac{1}{r_{e1}^2 r_{12}^2} \frac{\partial}{\partial(2r_{e1}+2r_{12})} \right. \\
 &\quad \left. \times \int_0^\infty \cos k(2r_{e1}+2r_{12}) \exp\left(-\frac{\lambda^2 k^2}{2}\right) dk + \frac{1}{r_{e2}^2 r_{12}^2} \frac{\partial}{\partial(2r_{e2}+2r_{12})} \int_0^\infty \cos k(2r_{e2}+2r_{12}) \exp\left(-\frac{\lambda^2 k^2}{2}\right) dk \right] \\
 &= (2\pi)^{3/2} \left\{ \frac{1}{\lambda^3} + \frac{a}{\lambda} \left[\frac{1}{r_{e1}^2} \frac{\partial}{\partial(2r_{e1})} \exp\left(-\frac{(2r_{e1})^2}{2\lambda^2}\right) + \frac{1}{r_{e2}^2} \frac{\partial}{\partial(2r_{e2})} \exp\left(-\frac{(2r_{e2})^2}{2\lambda^2}\right) \right] \right. \\
 &\quad - \frac{a^2}{\lambda} \left[\frac{2}{r_{e1}r_{12}r_{e2}} \frac{\partial}{\partial(r_{e1}+r_{12}+r_{e2})} \exp\left(-\frac{(r_{e1}+r_{12}+r_{e2})^2}{2\lambda^2}\right) + \frac{1}{r_{e1}^2} \frac{\partial^2}{\partial(2r_{e1})^2} \exp\left(-\frac{(2r_{e1})^2}{2\lambda^2}\right) \right. \\
 &\quad \left. + \frac{1}{r_{e2}^2} \frac{\partial^2}{\partial(2r_{e2})^2} \exp\left(-\frac{(2r_{e2})^2}{2\lambda^2}\right) \right] + \frac{a^3}{\lambda} \left[\frac{1}{r_{e1}^2 r_{12}^2} \frac{\partial}{\partial(2r_{e1}+2r_{12})} \exp\left(-\frac{(2r_{e1}+2r_{12})^2}{2\lambda^2}\right) \right. \\
 &\quad \left. + \frac{1}{r_{e2}^2 r_{12}^2} \frac{\partial}{\partial(2r_{e2}+2r_{12})} \exp\left(-\frac{(2r_{e2}+2r_{12})^2}{2\lambda^2}\right) + \frac{4}{r_{e1}r_{12}r_{e2}} \frac{\partial^2}{\partial(r_{e1}+r_{12}+r_{e2})^2} \exp\left(-\frac{(r_{e1}+r_{12}+r_{e2})^2}{2\lambda^2}\right) \right. \\
 &\quad \left. \left. + \frac{2}{3r_{e1}^2} \frac{\partial^3}{\partial(2r_{e1})^3} \exp\left(-\frac{(2r_{e1})^2}{2\lambda^2}\right) + \frac{2}{3r_{e2}^2} \frac{\partial^3}{\partial(2r_{e2})^3} \exp\left(-\frac{(2r_{e2})^2}{2\lambda^2}\right) \right] \right\}. \quad (18)
 \end{aligned}$$

The first thing we notice about this expression is that the exponents of Gaussians are all *sums* of coordinates and never differences. The differences are all cancelled out when the angular integration of dk is performed. This is to be expected since, for large distances from the scattering centers, the matrix element should look like one from a single-scattering process. The next thing is that it would obviously be extremely convenient to have a simple notation for the above terms. This can be done easily in the following way. We draw a solid line to represent a "bond" of $1/r$ between the electron and a

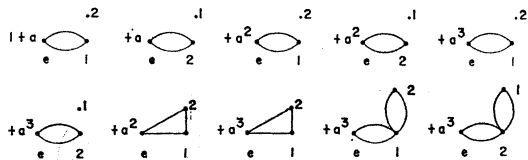


FIG. 1. Diagrams contributing to the coefficient of ρ^2 in ΔF .

helium atom or between two helium atoms. The number of coordinates in the Gaussian is given by the total number of bonds in the diagram and the number of derivatives is given by labeling the diagram with a power of a . Thus, for the second term considered above, we have the set of diagrams shown in Fig. 1.

When we consider the full semi-invariant, the first line of (unlinked) diagrams is zero. This is true in general. The second diagram on the second line is also unlinked but for a more subtle reason. This will be shown in Sec. VI. We are thus left with three diagrams contributing to $\rho^2 a^3$, which are shown in Fig. 2. These will be evaluated later along with the diagrams corresponding to the general case.

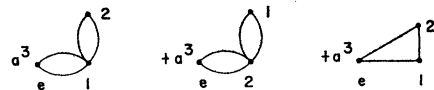


FIG. 2. Diagrams contributing to the coefficient of $\rho^2 a^3$ in ΔF .

V. COMBINATORICS (EVALUATION)

Before we can use the (diagram) notation established in the foregoing section, it is necessary to understand the algebra of operation of the original terms. In particular, we shall show that the combinatorial factor associated with a particular term is given by the number of ways of picking the points of the associated diagram from N points subject to restrictions caused by the symmetry of the diagram. In order to classify terms according to some semblance of order of magnitude, we first note that the terms in the second semi-invariant look just like those arising in the classical Coulomb problem (electron gas). This leads us to hope that we will find terms which look like ring (polarization) diagrams. However, we must be careful not to draw the analogy too closely.

Rather than try to compute $\Psi^*\Psi$ as we did in Sec. IV, we examine the coefficients A_i in the wave function. Expanding all the elements in A_1 in powers of ka , we have from Eq. (14)

$$A_1 = \frac{-ka \begin{vmatrix} 1 & \frac{a}{r_{12}} e^{ikr_{12}} \dots \frac{a}{r_{1n}} e^{ikr_{1n}} \\ e^{ik \cdot r_{12}} & 1 & \dots & \frac{a}{r_{2n}} e^{ikr_{2n}} \\ \vdots & & & \\ e^{ik \cdot r_{1n}} & \frac{a}{r_{2n}} e^{ikr_{2n}} \dots & & 1 \end{vmatrix}}{\begin{vmatrix} 1 & \frac{a}{r_{12}} e^{ikr_{12}} \dots \frac{a}{r_{1n}} e^{ikr_{1n}} \\ \frac{a}{r_{12}} e^{ikr_{12}} & 1 & \dots & \frac{a}{r_{2n}} e^{ikr_{2n}} \\ \vdots & & & \\ \frac{a}{r_{1n}} e^{ikr_{1n}} & \frac{a}{r_{12}} e^{ikr_{2n}} \dots & & 1 \end{vmatrix}} \quad (19)$$

Now, there are two types of terms which occur in $\Psi^*\Psi$, namely, terms which arise from the cross product of the plane wave and a spherical wave and terms which arise from the product of two spherical waves. Since we are looking for terms in which the exponential is the sum of all the coordinates involved, it is only necessary to look at the first class or what we shall call plane-wave terms. The second class of terms must necessarily contain at least one coordinate in the exponential which has the

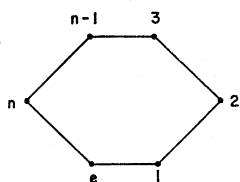


FIG. 3. Diagram for Eq. (21).

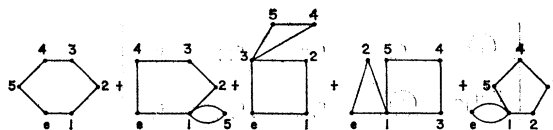


FIG. 4. Diagrams contributing to the coefficient of $\rho^5 a^6$ in ΔF .

opposite sign from the rest. Again, the $n=2$ term will make this clear. Upon examining Eq. (17) again and performing the angular integration of $\int dk$, as in Eq. (18), we see that the only contributing terms are the plane-wave terms. All other terms cancel those parts of the plane-wave terms in which the argument of the trigonometric function is not positive definite (or negative definite).

From the above argument and the semi-invariant theorem, we can find the terms of lowest order (i.e., lowest power of a) in $\Psi_{(n)}^* \Psi_{(n)}$. We first note that the semi-invariant theorem tells us that in order for a term in $\Psi_{(n)}^* \Psi_{(n)}$ to contribute to the trace (average), it must contain all n coordinates. Because of the structure of the coefficients A_i as ratios of determinants, the lowest power of a to contribute will be a^n and this will be obtained by making a "ring" in the determinant in the numerator, that is, for example, the term

$$\frac{e^{ik \cdot r_{12}} a^n}{r_{23} r_{34} \dots r_{n1}} \frac{e^{ikr_{e1}}}{r_{e1}} e^{-ik \cdot r_{e1}} + \text{c.c.}, \quad (20)$$

which leads to the term in the trace of

$$\rho^n a^n \int \dots \int \frac{1}{r_{e1} r_{12} r_{23} \dots r_{ne}} \frac{\partial}{\partial s} \exp\left(-\frac{s^2}{2\lambda^2}\right) \prod_{i=1}^N d\mathbf{r}_i = (\text{diagram in Fig. 3}), \quad (21)$$

where $s = r_{e1} + r_{12} + r_{23} + \dots + r_{ne}$. As mentioned before,

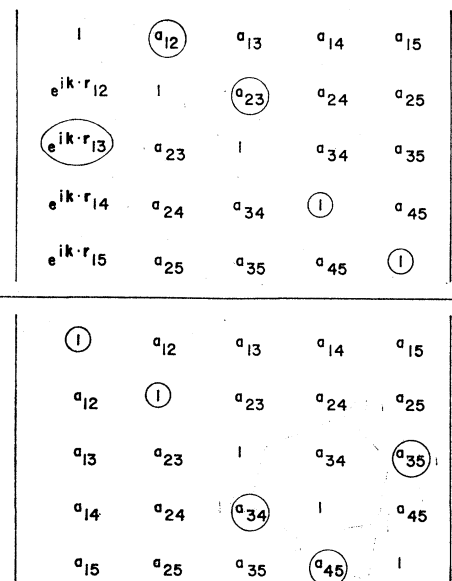


FIG. 5. Schematic representation of the algebraic term represented by Fig. 4(c). Factors in the term are circled.

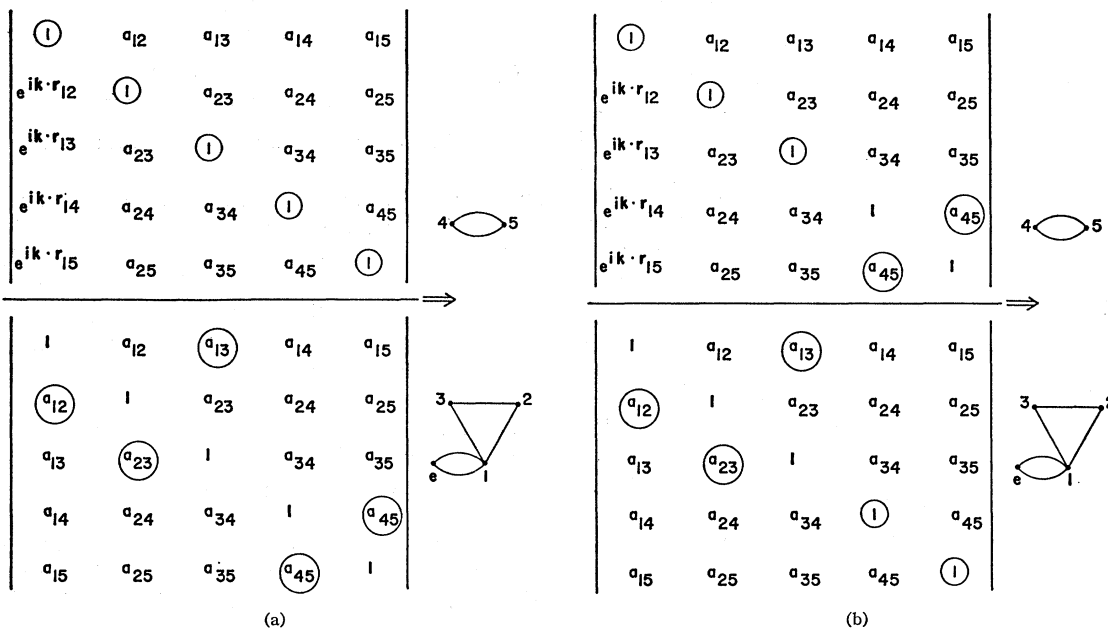


FIG. 6. Schematic representation of two irreducible terms contributing to the coefficient of $\rho^b a^a$. Factors in the terms are circled.

for the case of $n=2$, this term is cancelled by the full semi-invariant expression. (See Sec. VI.) The diagrams shown in Fig. 4 contribute to the coefficient of a^{n+1} . Figure 4 shows the case $n=5$ with the obvious extension to any n . These diagrams arise in the following way. (a) comes from taking a ring in the numerator and one power of ka in the denominator. The rest of the diagrams are formed by taking the appropriate ring in the numerator given by the part of the diagram containing the electron and a ring in the denominator given by the other part. For example, the term contributing to (c) is shown schematically by Fig. 5. All these diagrams are linked. Diagrams which are unlinked are zero because of cancellation between numerator and denominator. For example, the term given by Fig. 6(a) cancels the term given by Fig. 6(b) since they occur with opposite signs. This is obviously true in general. It remains only to find the combinatorial factor associated with each diagram and evaluate the most general type of integral in order to obtain an answer. By examining the determinants again, we can easily determine how many ways we can form a given term. This is the com-

binatorial factor. We find this in general for a diagram containing an electron loop with n vertices and a second loop with $m+1$ vertices as shown in Fig. 7. Such a diagram contributes to $\rho^{n+m} a^{n+m+1}$. Referring to Eq. (19) for A_1 , we see that the number of ways of obtaining an " n " loop in the numerator is $\binom{m+n-1}{n-2} (n-2)!$ while the number of ways of picking the appropriate loop in the denominator is $(n-1)(m+1)!$. Combining these, we get $(n-1)(m+n-1)!$ for the total number of ways of obtaining the diagram in Fig. 7. Now, there are $n+m$ plane-wave terms coming from the $n+m$ coefficients A_i and a factor of $1/(n+m)!$ which comes from the $(n+m)$ multiple summation over all N helium atoms. This is actually the number of ways of picking $n+m$ helium atoms from N helium atoms, that is,

$$\sum_{i_1 < i_2 < i_3 < \dots < i_{n+m}} \frac{N(N-1)(N-2) \dots (N-n-m)}{(n+m)!} \approx \frac{N^{n+m}}{(n+m)!}. \quad (22)$$

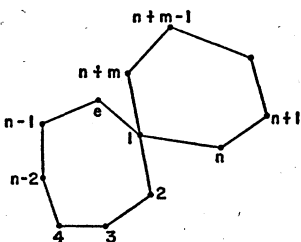


FIG. 7. Typical diagram contributing to the coefficient of $\rho^{n+m} a^{n+m+1}$.

Consequently, the combinatorial factor for the diagram is $n-1$ or the number of ways of attaching the helium loop onto the electron loop. For a single-loop diagram with n helium atoms, the combinatorial factor is clearly n since this is the number of ways of picking the extra ka in the denominator.

Evaluation of the integrals poses a more difficult problem. In the first place, the contribution of each

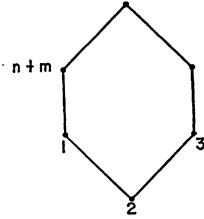


FIG. 8. Diagram for Eq. (23).

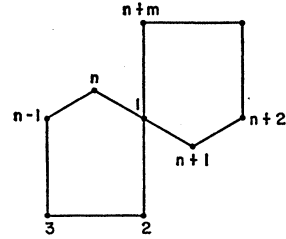


FIG. 9. Diagram for Eq. (24).

diagram in a given order $\rho^n a^{n+1}$ is clearly proportional to λ^{2n-1} . If we look at the whole series, we now have an expansion of the free energy in powers of β or $1/kT$. This would be highly undesirable since we are interested in the low-temperature behavior of the free energy. However, it is to be expected that analytic continuation of the series would yield an expression which is valid in the low-temperature region as in the classical Coulomb problem with a cutoff which becomes infinite.

Referring to Fig. 4 and generalizing to the N th term, we see that the following two types of integrals must be evaluated:

$$\begin{aligned} \text{(Diagram in Fig. 8)} &= \int \cdots \int \frac{1}{r_{12} r_{23} \cdots r_{n+m1}} \\ &\times \frac{\partial^2}{\partial s^2} \exp\left(-\frac{s^2}{2\lambda^2}\right) \prod_{i=1}^{n+m} d\mathbf{r}_i \quad (23) \end{aligned}$$

and

$$\begin{aligned} \text{(Diagram in Fig. 9)} &= \int \cdots \int \frac{1}{r_{12} r_{23} \cdots r_{n1} r_{1n+1} \cdots r_{n+m1}} \\ &\times \frac{\partial}{\partial s} \exp\left(-\frac{s^2}{2\lambda^2}\right) \prod_{i=1}^{n+m} d\mathbf{r}_i, \quad (24) \end{aligned}$$

where s in both cases is $\sum r_{ij}$. Actually, it is not neces-

sary to evaluate Eq. (24) alone but rather

$$\begin{aligned} \sum_{n=2}^{N-1} \int \cdots \int \frac{n-1}{r_{12} r_{23} \cdots r_{n1} r_{1n+1} \cdots r_{N1}} \\ \times \frac{\partial}{\partial s} \exp\left(-\frac{s^2}{2\lambda^2}\right) \prod_{i=1}^N d\mathbf{r}_i. \quad (25) \end{aligned}$$

As shown in Sec. VI, the sum of Eqs. (23) and (25) is zero. Thus, the only term contributing to the free energy from s -wave scattering including all multiple-scattering effects is $2\pi\rho a(\hbar^2/m)$. This is also the ground-state energy for the system.

VI. INTEGRATION (EVALUATION)

We have to evaluate the integrals of general form represented by

$$\int \cdots \int \frac{1}{r_{12} r_{23} \cdots r_{N1}} \frac{\partial}{\partial s} \exp\left(-\frac{s^2}{2\lambda^2}\right) \prod_{i=1}^N d\mathbf{r}_i, \quad (26)$$

$$\int \cdots \int \frac{1}{r_{12} r_{23} \cdots r_{N1}} \frac{\partial^2}{\partial s^2} \exp\left(-\frac{s^2}{2\lambda^2}\right) \prod_{i=1}^N d\mathbf{r}_i, \quad (27)$$

$$\begin{aligned} \int \cdots \int \frac{1}{r_{12} r_{23} \cdots r_{n1} r_{1n+1} \cdots r_{n+m1}} \\ \times \frac{\partial}{\partial s} \exp\left(-\frac{s^2}{2\lambda^2}\right) \prod_{i=1}^{n+m} d\mathbf{r}_i. \quad (28) \end{aligned}$$

The integral of Eq. (26) is first rewritten as

$$\int \cdots \int \frac{1}{r_{12} r_{23} \cdots r_{N1}} \frac{\partial}{\partial s} \exp\left(-\frac{s^2}{2\lambda^2}\right) \prod_{i=1}^N d\mathbf{r}_i = -\frac{\Omega}{\lambda^2} \int \cdots \int \frac{s}{r_{12} r_{23} \cdots r_{N1}} \exp\left(-\frac{s^2}{2\lambda^2}\right) d\mathbf{r}_{12} d\mathbf{r}_{23} \cdots d\mathbf{r}_{N-1N}, \quad (29)$$

where we have gone to relative coordinates in the integral and Ω is the volume of the system. The integral is now evaluated using the Fourier integral theorem by "opening" the ring at one point, taking the Fourier transform and integrating the Fourier transform.

$$\begin{aligned} &\int \cdots \int \frac{s}{r_{12} r_{23} \cdots r_{N1}} \exp\left(-\frac{s^2}{2\lambda^2}\right) d\mathbf{r}_{12} d\mathbf{r}_{23} \cdots d\mathbf{r}_{N-1N} \\ &= \frac{1}{8\pi^3} \int \cdots \int \frac{s}{r_{12} r_{13} \cdots r_{NN'}} \exp\left(-\frac{s^2}{2\lambda^2}\right) e^{i\mathbf{k} \cdot \mathbf{r}_{N'1}} d\mathbf{r}_{12} d\mathbf{r}_{23} \cdots d\mathbf{r}_{N-1N} d\mathbf{r}_{N'1} d\mathbf{k} \\ &= \frac{(4\pi)^N}{8\pi^3} \int \frac{1}{k^N} \int_0^\infty \cdots \int_0^\infty s \exp\left(-\frac{s^2}{2\lambda^2}\right) \sin kr_{12} \sin kr_{23} \cdots \sin kr_{N-1N} \sin kr_{NN'} d\mathbf{r}_{12} d\mathbf{r}_{23} \cdots d\mathbf{r}_{N-1N} d\mathbf{r}_{NN'} d\mathbf{k} \\ &\equiv \frac{(4\pi)^N}{8\pi^3} \int I^{(N)}(k, \lambda) d\mathbf{k}. \quad (30) \end{aligned}$$

Let us now examine the multiple integral $I^{(N)}$ for $N=2$ and 3.

$$\begin{aligned}
I^{(2)} &= \frac{1}{k^2} \int_0^\infty \int_0^\infty (r_1+r_2) \exp\left(-\frac{(r_1+r_2)^2}{2\lambda^2}\right) \operatorname{sink}r_1 \operatorname{sink}r_2 dr_1 dr_2 \\
&= \frac{1}{k^2} \int_0^\infty \int_0^s s \exp\left(-\frac{s^2}{2\lambda^2}\right) \operatorname{sink}t \operatorname{sink}(s-t) dt ds \\
&= \frac{1}{2k^2} \int_0^\infty \int_0^s s \exp\left(-\frac{s^2}{2\lambda^2}\right) [\operatorname{cosk}(s-2t) - \operatorname{cosks}] dt ds \\
&= \frac{1}{2k^2} \int_0^\infty s \exp\left(-\frac{s^2}{2\lambda^2}\right) \left[\frac{\operatorname{sinks}}{k} - s \operatorname{cosks}\right] ds \\
&= \frac{1}{2k^2} \left(\frac{1}{k} \frac{\partial}{\partial k}\right) \int_0^\infty s \exp\left(-\frac{s^2}{2\lambda^2}\right) \operatorname{sinks} ds \\
&= \lambda^3 \frac{(2\pi)^{1/2}}{2} f^{(2)}\left(k, \frac{\partial}{\partial k}\right) k \exp\left(-\frac{k^2\lambda^2}{2}\right), \tag{31}
\end{aligned}$$

where we have changed variables to $s=r_1+r_2$ and $t=r_1$. The polynomial operator $f^{(2)}(k, \partial/\partial k)$ is defined by Eq. (31). To evaluate $I^{(3)}$, we change variables to $s=r_1+r_2+r_3$, $t=r_1+r_2$ and $r=r_1$ and find

$$I^{(3)} = \lambda^3 \frac{(2\pi)^{1/2}}{2} f^{(3)}\left(k, \frac{\partial}{\partial k}\right) k \exp\left(-\frac{k^2\lambda^2}{2}\right), \tag{32}$$

where

$$f^{(3)} = \frac{1}{8k^3} \left(\frac{3}{k^2} \frac{\partial}{\partial k} + \frac{\partial^2}{\partial k^2} \right). \tag{33}$$

Clearly, $I^{(N)}$ can be written as

$$I^{(N)} = \lambda^3 \frac{(2\pi)^{1/2}}{2} f^{(N)} k \exp\left(-\frac{k^2\lambda^2}{2}\right). \tag{34}$$

Rather than evaluate the coefficients of the polynomial operator $f^{(N)}$, we only have to evaluate the result of $f^{(N)}$ acting on $k \exp(-k^2\lambda^2/2)$. To do this, we write

$$\begin{aligned}
f^{(N)} k \exp(-k^2\lambda^2/2) &= -\frac{1}{\lambda^2} f^{(N)} \frac{\partial}{\partial k} \exp\left(-\frac{k^2\lambda^2}{2}\right) \\
&= -\frac{1}{\lambda^2} \times \frac{2}{\lambda(2\pi)^{1/2}} f^{(N)} \frac{\partial}{\partial k} \int_0^\infty \exp\left(-\frac{s^2}{2\lambda^2}\right) \operatorname{cosks} ds \\
&= \frac{2}{\lambda^3(2\pi)^{1/2}} f^{(N)} \int_0^\infty s \exp\left(-\frac{s^2}{2\lambda^2}\right) \operatorname{sinks} ds \\
&= \frac{2}{\lambda^3(2\pi)^{1/2}} \frac{1}{k^N} \int_0^\infty \cdots \int_0^\infty s \exp\left(-\frac{s^2}{2\lambda^2}\right) \operatorname{sink}r_1 \operatorname{sink}r_2 \cdots \operatorname{sink}r_N \prod_{i=1}^N dr_i \\
&= \frac{2}{\lambda^3(2\pi)^{1/2}} \frac{1}{k} \int_0^\infty \int_0^\infty s \exp\left(-\frac{s^2}{2\lambda^2}\right) \operatorname{sink}r_1 f^{(N-1)}\left(k, \frac{\partial}{\partial k}\right) \operatorname{sinks}' dr_1 ds' \\
&= \frac{2}{\lambda^3(2\pi)^{1/2}} \lim_{k' \rightarrow k} \frac{1}{k'} f^{(N-1)}\left(k, \frac{\partial}{\partial k}\right) \int_0^\infty \int_0^\infty s \exp\left(-\frac{s^2}{2\lambda^2}\right) \operatorname{sink}'r_1 \operatorname{sinks}' dr_1 ds' \\
&= \frac{2}{\lambda^3(2\pi)^{1/2}} \lim_{k' \rightarrow k} \frac{1}{k'} f^{(N-1)}\left(k, \frac{\partial}{\partial k}\right) \int_0^\infty \int_0^s s \exp\left(-\frac{s^2}{2\lambda^2}\right) \\
&\quad \times \frac{1}{2} [\operatorname{cos}(ks - (k+k')r) - \operatorname{cos}(ks + (k'-k)r)] dr ds
\end{aligned}$$

$$\begin{aligned}
 &= \frac{2}{\lambda^3(2\pi)^{1/2}} \lim_{k' \rightarrow k} \frac{1}{k'} f^{(N-1)}\left(k, \frac{\partial}{\partial k}\right) \int_0^\infty s \exp\left(-\frac{s^2}{2\lambda^2}\right) \frac{1}{k^2 - k'^2} (k \sin k's - k' \sin ks) ds \\
 &= \frac{2}{\lambda^3(2\pi)^{1/2}} \lim_{k' \rightarrow k} \frac{1}{k'} f^{(N-1)}\left(k, \frac{\partial}{\partial k}\right) \frac{1}{k^2 - k'^2} \int_0^\infty \left[k' \frac{\partial}{\partial k} \cos ks - k \frac{\partial}{\partial k'} \cos k's \right] \exp\left(-\frac{s^2}{2\lambda^2}\right) ds \\
 &= \lim_{k' \rightarrow k} \frac{1}{k'} f^{(N-1)}\left(k, \frac{\partial}{\partial k}\right) \frac{kk'}{k'^2 - k^2} \left[\exp\left(-\frac{k^2\lambda^2}{2}\right) - \exp\left(-\frac{k'^2\lambda^2}{2}\right) \right] \\
 &= \lim_{k' \rightarrow k} f^{(N-1)}\left(k, \frac{\partial}{\partial k}\right) k \exp\left(-\frac{k^2\lambda^2}{2}\right) \frac{[1 - \exp(-(k'^2 - k^2)\lambda^2/2)]}{k'^2 - k^2}. \tag{35}
 \end{aligned}$$

Now define

$$J^{(N)}(k, k'; \lambda, \lambda') = f^{(N-1)}\left(k, \frac{\partial}{\partial k}\right) k \exp\left(-\frac{k^2\lambda^2}{2}\right) \frac{[1 - \exp(-(k'^2 - k^2)\lambda'^2/2)]}{k'^2 - k^2}; \tag{36}$$

then

$$\frac{\partial J}{\partial \lambda'} = \lambda' f^{(N-1)}\left(k, \frac{\partial}{\partial k}\right) k \exp\left(-\frac{k^2(\lambda^2 - \lambda'^2)}{2}\right) \exp\left(-\frac{k'^2\lambda'^2}{2}\right). \tag{37}$$

Clearly, $f^{(N)}$ acting on $k \exp(-k^2\lambda^2/2)$ yields a polynomial of the form

$$\sum_{n=1}^N a_n \frac{\lambda^{2(n-1)}}{k^{(N-n)}} = P^{(N)}(k^2, \lambda^2)$$

times $\exp(-k^2\lambda^2/2)$. Therefore

$$\begin{aligned}
 \lim_{\substack{k' \rightarrow k \\ \lambda' \rightarrow \lambda}} J^{(N)}(k, k'; \lambda, \lambda') &= \lim_{k' \rightarrow k} \int_0^\lambda \lambda' f^{(N-1)}\left(k, \frac{\partial}{\partial k}\right) k \exp\left(-\frac{k^2(\lambda^2 - \lambda'^2)}{2}\right) \exp\left(-\frac{k'^2\lambda'^2}{2}\right) d\lambda' \\
 &= \int_0^\lambda \lambda' P^{(N-1)}(k^2, \lambda^2 - \lambda'^2) \exp\left(-\frac{k^2\lambda^2}{2}\right) d\lambda' \\
 &= Q^{(N-1)}(k^2, \lambda^2) \exp(-k^2\lambda^2/2), \tag{38}
 \end{aligned}$$

where $Q^{(N)}$ is also a polynomial with N terms. But $Q^{(N-1)}$ must be equal to $P^{(N)}$; therefore $P^{(N)}$ can contain only one term and from $P^{(2)}$, we see that this term is the highest power of λ^2 , namely, $a_N \lambda^{2(N-1)}$. From Eq. (38), we immediately get the recursion relation

$$a_N = (1/2(N-1))a_{N-1}, \tag{39}$$

so that we have finally

$$\lim_{\substack{k' \rightarrow k \\ \lambda' \rightarrow \lambda}} J^{(N)}(k, k'; \lambda, \lambda') = f^{(N)} k \exp\left(-\frac{k^2\lambda^2}{2}\right) = \frac{\lambda^{2(N-1)}}{2^{N-1}(N-1)!} \exp\left(-\frac{k^2\lambda^2}{2}\right), \tag{40}$$

since $a_1 = 1$. Returning to Eq. (29), we have

$$\begin{aligned}
 \int \dots \int \frac{1}{r_{12} r_{23} \dots r_{N1}} \frac{\partial}{\partial s} \exp\left(-\frac{s^2}{2\lambda^2}\right) \prod_{i=1}^N d\mathbf{r}_i &= -\frac{\Omega (4\pi)^N}{\lambda^2 8\pi^3} \int I^N(k, \lambda) d\mathbf{k} \\
 &= -\frac{\Omega (4\pi)^N}{\lambda^2 8\pi^3} \lambda^3 \frac{(2\pi)^{1/2}}{2} \frac{\lambda^{2(N-1)}}{2^{N-1}(N-1)!} \frac{(2\pi)^{3/2}}{\lambda^3} \\
 &= -\Omega (2\pi)^{N-1} \frac{\lambda^{2(N-2)}}{(N-1)!}. \tag{41}
 \end{aligned}$$

Finally, we see that the diagram in Fig. 10 takes the form

$$\begin{aligned}
 & (-1)^n (2\pi)^n \frac{\rho^n a^n \lambda^{2n}}{n!} \\
 &= \frac{(-2\pi \rho a \lambda^2)^n}{n!} \\
 &= \frac{1}{n!} (e \quad 1)^n \\
 &= \sum_{i_1 < i_2 < i_3 \dots i=n}^N \langle f_{i_1} \rangle \langle f_{i_2} \rangle \dots \langle f_{i_n} \rangle. \tag{42}
 \end{aligned}$$

Thus, the term represented by Eq. (42) is unlinked and the full semi-invariant expression is zero. We now turn to the integral of Eq. (27). It is first rewritten as

$$\begin{aligned}
 & \int \dots \int \frac{1}{r_{12} r_{23} \dots r_{N1}} \frac{\partial^2}{\partial s^2} \exp\left(-\frac{s^2}{2\lambda^2}\right) \prod_{i=1}^N dx_i \\
 &= \int \dots \int \frac{1}{r_{12} r_{23} \dots r_{N1}} \left(\frac{s}{\lambda^2} - \frac{1}{\lambda^2}\right) \exp\left(-\frac{s^2}{2\lambda^2}\right) \prod_{i=1}^N dx_i \\
 &= \frac{1}{\lambda^2} \left[\lambda \frac{\partial}{\partial \lambda} \int \dots \int \frac{1}{r_{12} r_{23} \dots r_{N1}} \exp\left(-\frac{s^2}{2\lambda^2}\right) \prod_{i=1}^N dx_i - \int \dots \int \frac{1}{r_{12} r_{23} \dots r_{N1}} \exp\left(-\frac{s^2}{2\lambda^2}\right) \prod_{i=1}^N dx_i \right] \\
 &= \frac{\Omega}{\lambda^2} \left(\lambda \frac{\partial}{\partial \lambda} - 1 \right) \int \dots \int \frac{1}{r_{12} r_{23} \dots r_{N1}} \exp\left(-\frac{s^2}{2\lambda^2}\right) dx_{12} dx_{23} \dots dx_{N-1N} \\
 &= \frac{(2N-4)\Omega}{\lambda^2} \int \dots \int \frac{1}{r_{12} r_{23} \dots r_{N1}} \exp\left(-\frac{s^2}{2\lambda^2}\right) dx_{12} dx_{23} \dots dx_{N-1N}. \tag{43}
 \end{aligned}$$

The integral is now evaluated as before by opening the ring at one point, taking the Fourier transform and integrating the Fourier transform.

$$\begin{aligned}
 & \int \dots \int \frac{1}{r_{12} r_{23} \dots r_{N1}} \exp\left(-\frac{s^2}{2\lambda^2}\right) dx_{12} dx_{23} \dots dx_{N-1N} \\
 &= \frac{1}{8\pi^3} \int \dots \int \frac{1}{r_{12} r_{23} \dots r_{NN'}} \exp\left(-\frac{s^2}{2\lambda^2}\right) e^{i\mathbf{k} \cdot \mathbf{r}_{N'1}} dx_{12} dx_{23} \dots dx_{NN'} d\mathbf{k} \\
 &= \frac{1}{8\pi^3} \int \dots \int \frac{1}{r_{12} r_{23} \dots r_{NN'}} \exp\left(-\frac{s^2}{2\lambda^2}\right) e^{i\mathbf{k} \cdot \mathbf{r}_{12}} e^{i\mathbf{k} \cdot \mathbf{r}_{23}} \dots e^{i\mathbf{k} \cdot \mathbf{r}_{NN'}} dx_{12} dx_{23} \dots dx_{NN'} d\mathbf{k} \\
 &= \frac{(4\pi)^N}{8\pi^3} \int \frac{1}{k^N} \int_0^\infty \dots \int_0^\infty \exp\left(-\frac{s^2}{2\lambda^2}\right) \sin kr_{12} \sin kr_{23} \dots \sin kr_{NN'} dx_{12} dx_{23} \dots dx_{NN'} d\mathbf{k} \\
 &= \frac{(4\pi)^N}{8\pi^3} \int f^{(n)}\left(k, \frac{\partial}{\partial k}\right) \int_0^\infty \exp\left(-\frac{s^2}{2\lambda^2}\right) \sin ks ds d\mathbf{k} \\
 &= \frac{(4\pi)^N}{8\pi^3} \int \lambda f^{(n)} \exp\left(-\frac{k^2 \lambda^2}{2}\right) \int_0^{k\lambda} \exp\left(-\frac{x^2}{2}\right) dx d\mathbf{k} \\
 &\equiv \frac{(4\pi)^N}{8\pi^3} \lambda \int J^{(N)}(k, \lambda) d\mathbf{k}. \tag{44}
 \end{aligned}$$

To find $J^{(N)}(k, \lambda)$, we use the following trick: First define

$$J^{(N)}(k; \lambda, \lambda') = f^{(N)}\left(k, \frac{\partial}{\partial k}\right) \exp\left(-\frac{k^2}{2\lambda^2}\right) \int_0^{k\lambda'} \exp\left(\frac{x^2}{2}\right) dx; \tag{45}$$

then

$$\begin{aligned} \frac{\partial J^{(N)}}{\partial \lambda'} &= f^{(N)}\left(k, \frac{\partial}{\partial k}\right) k \exp\left(-\frac{k^2(\lambda^2 - \lambda'^2)}{2}\right) \\ &= \frac{(\lambda^2 - \lambda'^2)^{N-1}}{2^{N-1}(N-1)!} \exp\left(-\frac{k^2(\lambda'^2 - \lambda^2)}{2}\right). \end{aligned} \tag{46}$$

We cannot simply integrate Eq. (46) to obtain $J^{(N)}$. However, since we are only interested in $\int J^{(N)} d^3k$, we do this first.

$$\begin{aligned} \int J^{(N)}(k, \lambda) d\mathbf{k} &= \int \lim_{\lambda' \rightarrow \lambda} J^{(N)}(k; \lambda, \lambda') d\mathbf{k} \\ &= \int_0^\lambda \int \frac{\partial J^{(N)}}{\partial \lambda'} d\mathbf{k} d\lambda' \\ &= \int_0^\lambda (2\pi)^{3/2} \frac{\lambda}{2^{N-1}(N-1)!} (\lambda^2 - \lambda'^2)^{N-5/2} d\lambda' \\ &= \frac{\lambda^{2N-3} (2\pi)^{3/2}}{2^{N-1}(N-1)!} \frac{(2N-5)(2N-7)\cdots 3 \times 1 \pi}{(2N-4)(2N-6)\cdots 4 \times 2 \cdot 2}. \end{aligned} \tag{47}$$

Thus, we have

$$\int \cdots \int \frac{1}{r_{12} r_{23} \cdots r_{N1}} \frac{\partial^2}{\partial s^2} \exp\left(-\frac{s^2}{2\lambda^2}\right) \prod_{e=i}^N d\mathbf{r}_i = \frac{\Omega \lambda^{2N-5} (4\pi)^N}{2^{2N-4}(N-1)!(N-3)!} \frac{(2\pi)^{3/2} \pi}{8\pi^3} (2N-5)(2N-7)\cdots 3 \times 1. \tag{48}$$

To evaluate the integral of Eq. (28), we use the same kind of trick.

$$\begin{aligned} &\int \cdots \int \frac{1}{r_{12} r_{23} \cdots r_{n1} r_{1n+1} \cdots r_{n+m1}} \frac{\partial}{\partial s} \exp\left(-\frac{s^2}{2\lambda^2}\right) \prod_{e=1}^{n+m} d\mathbf{r}_i \\ &= -\frac{\Omega}{(8\pi^3)^2 \lambda^2} \int \cdots \int \frac{1}{r_{12} r_{23} \cdots r_{nn'} r_{1n+1} \cdots r_{n+m(n+m)'}} s \exp\left(-\frac{s^2}{2\lambda^2}\right) \\ &\quad \times e^{i\mathbf{k} \cdot \mathbf{r}_{n1}} e^{i\mathbf{k}' \cdot \mathbf{r}_{(n+m)'1}} d\mathbf{r}_{12} \cdots d\mathbf{r}_{nn'} d\mathbf{r}_{1n+1} \cdots d\mathbf{r}_{n+m(n+m)'} d\mathbf{k} d\mathbf{k}' \\ &= -\frac{\Omega (4\pi)^{n+m+1}}{(8\pi^3)^2 \lambda^2} \iint \frac{1}{k^n k'^{m+1}} \int_0^\infty \cdots \int_0^\infty s \exp\left(-\frac{s^2}{2\lambda^2}\right) \text{sink} r_{12} \cdots \text{sink} r_{nn'} \text{sink}' r_{1n+m} \text{sink}' r_{n+m(n+m)'} \\ &\quad \times dr_{12} \cdots dr_{nn'} dr_{1n+1} \cdots dr_{n+m(n+m)'} d\mathbf{k} d\mathbf{k}' \\ &= -\frac{\Omega (4\pi)^{n+m+1}}{(8\pi^3)^2 \lambda^2} \iint f^{(n)}\left(k, \frac{\partial}{\partial k}\right) f^{(m+1)}\left(k', \frac{\partial}{\partial k'}\right) \int_0^\infty \int_0^\infty s \exp\left(-\frac{s^2}{2\lambda^2}\right) \text{sink} r_1 \text{sink}' r_2 dr_1 dr_2 d\mathbf{k} d\mathbf{k}' \\ &= -\frac{\Omega (4\pi)^{n+m+1} \lambda^3 (2\pi)^{1/2}}{(8\pi^3)^2 \lambda^2} \iint f^{(n)}\left(k, \frac{\partial}{\partial k}\right) f^{(m+1)}\left(k', \frac{\partial}{\partial k'}\right) \frac{k k' \exp(-k^2 \lambda^2 / 2)}{k'^2 - k^2} \left[1 - \exp\left(-\frac{(k'^2 - k^2) \lambda^2}{2}\right)\right] d\mathbf{k} d\mathbf{k}' \\ &= -\frac{\Omega (4\pi)^{n+m+1} \lambda^3 (2\pi)^{1/2}}{(8\pi^3)^2 \lambda^2} \iint H^{(n, m+1)}(k, k'; \lambda) d\mathbf{k} d\mathbf{k}' \end{aligned} \tag{49}$$

using Eq. (35). Again define

$$H^{(n,m+1)}(k,k';\lambda,\lambda') \equiv f^{(n)}\left(k, \frac{\partial}{\partial k}\right) f^{(m+1)}\left(k', \frac{\partial}{\partial k'}\right) k k' \exp\left(-\frac{k^2 \lambda^2}{2}\right) \frac{[1 - \exp(-(k'^2 - k^2)\lambda'/2)]}{k'^2 - k^2} \tag{50}$$

and take the derivative:

$$\begin{aligned} \frac{\partial H}{\partial \lambda'} &= \lambda' f^{(n)}\left(k, \frac{\partial}{\partial k}\right) f^{(m+1)}\left(k', \frac{\partial}{\partial k'}\right) k k' \exp\left(-\frac{k'^2 \lambda'^2}{2}\right) \exp\left(-\frac{k^2(\lambda^2 - \lambda'^2)}{2}\right) \\ &= \frac{\lambda'^{2n-1}(\lambda'^2 - \lambda^2)^m}{2^{n+m+1}(n-1)!m!} \exp\left(-\frac{k'^2 \lambda'^2}{2}\right) \exp\left(-\frac{k^2(\lambda^2 - \lambda'^2)}{2}\right) \end{aligned} \tag{51}$$

using Eq. (40). As before, we integrate on k and k' before integrating on λ' . This gives

$$\begin{aligned} \int H(k,k';\lambda) d\mathbf{k} d\mathbf{k}' &= \int_0^\lambda \int \frac{\partial H(k,k';\lambda,\lambda')}{\partial \lambda'} d\mathbf{k} d\mathbf{k}' d\lambda' \\ &= \int_0^\lambda \frac{8\pi^3}{2^{n+m-1}(n-1)!m!} \lambda'^{2n-4} (\lambda'^2 - \lambda^2)^{m-3/2} d\lambda' \\ &= \frac{8\pi^3 \lambda^{2(n+m)-6}}{2^{n+m+1}(n-1)!m!} \int_0^{\pi/2} (\sin\theta)^{2n-4} (\cos\theta)^{2m-2} d\theta. \end{aligned} \tag{52}$$

Rather than evaluate this integral alone, we evaluate

$$\sum_{n=2}^{N-1} (n-1) H^{(n,N+1-n)}(k,k';\lambda) d\mathbf{k} d\mathbf{k}'$$

as given by Eq. (25).

$$\begin{aligned} \sum_{n=2}^{N-1} (n-1) \int H^{(n,N+1-n)}(k,k';\lambda) d\mathbf{k} d\mathbf{k}' &= \frac{8\pi^3 \lambda^{2N-6}}{2^{N-1}(N-1)!} \int_0^{\pi/2} \sum_{n=2}^{N-1} \frac{(n-1)(N-1)!}{(n-1)!(N-n)!} (\sin^2\theta)^{n-2} (\cos^2\theta)^{N-n-1} d\theta \\ &= \frac{8\pi^3 \lambda^{2N-8}}{2^{N-1}(N-1)!} \int_0^{\pi/2} \frac{1}{\cos^2\theta} \frac{\partial}{\partial \sin^2\theta} \sum_{n=2}^{N-1} \binom{N-1}{n-1} (\sin^2\theta)^{n-1} (\cos^2\theta)^{N-n} d\theta \\ &= \frac{8\pi^3 \lambda^{2N-6}}{2^{N-1}(N-1)!} \int_0^{\pi/2} \frac{1}{\cos^2\theta} \frac{\partial}{\partial \sin^2\theta} [(\sin^2\theta + \cos^2\theta)^{N-1} - (\sin^2\theta)^{N-1} - (\cos^2\theta)^{N-1}] d\theta \\ &= \frac{8\pi^3 \lambda^{2N-6}}{2^{N-1}(N-1)!} (N-1) \int_0^{\pi/2} \frac{1}{\cos^2\theta} [1 - (\sin^2\theta)^{N-2}] d\theta \\ &= \frac{8\pi^3 \lambda^{2N-6}}{2^{N-1}(N-1)!} (N-1) \int_0^{\pi/2} [1 + \sin^2\theta + \sin^4\theta + \dots + (\sin^2\theta)^{N-3}] d\theta \\ &= \frac{8\pi^3 \lambda^{2N-6}}{2^{N-1}(N-2)!} \left[\sum_{n=1}^{N-3} \frac{(2n-1)(2n-3) \times \dots \times 3 \times 1}{(2n)(2n-2) \times \dots \times 4 \times 2} + 1 \right] \frac{\pi}{2} \\ &= \frac{8\pi^3 \lambda^{2N-6}}{2^{N-1}(N-2)!} \frac{(2N-5)(2N-7) \dots 3 \times 1}{2^{N-3}(N-3)!} \frac{\pi}{2}. \end{aligned} \tag{53}$$

Finally, we have

$$\sum_{n=2}^{N-1} (n-1) \int \cdots \int \frac{1}{r_{12} r_{23} \cdots r_{n1} r_{1n+1} \cdots r_{N1}} \frac{\partial}{\partial s} \exp\left(-\frac{s^2}{2\lambda^2}\right) \prod_{i=1}^N dx_i$$

$$= -\frac{\Omega \lambda^{2N-5} (4\pi)^N (2\pi)^{3/2} \pi}{2^{2N-4} (N-2)! (N-3)! 8\pi^3 2} (2N-5)(2N-7) \cdots \times 3 \times 1. \quad (54)$$

Comparing with Eq. (48) and remembering that the combinatorial factor for that term is $N-1$, we see that the sum of the two integrals is zero.

VII. CONCLUSIONS

We must now regard the above result as a theorem: The free energy of a particle interacting with a system of hard-core scattering centers is given in the s -wave approximation by $2\pi\rho a(\hbar^2/m)$ including all multiple-scattering effects. To obtain a better approximation, one must use p -wave terms in the wave function [Eq. (12)]. For the electron in helium, the s -wave approximation is sufficient; it shows that at the appropriate density,⁶ the free energy can be lowered by changing

⁶ By assuming the electron trapped in a well of depth $2\pi\rho a\hbar^2/m$ and radius R , one finds easily, by balancing the zero-point energy of the electron against PV for the helium gas, R as a function of density and consequently the free energy of the electron at zero degrees as a function of density. The density at which the zero-point energy becomes less than $2\pi\rho a\hbar^2/m$ is about $\frac{1}{2}$ the saturation density at $T=4^\circ$ and a saturation pressure of one atmosphere.

to a "bubble" configuration. For the problem of more general interest, namely, the hard-sphere Bose fluid, it is certainly necessary to include higher order scattering terms as well as the effect of statistics although it is by no means evident how to do this consistently. Finally, it should be mentioned that the method used here is just the converse of the pseudopotential method for hard spheres since we are replacing a potential-scattering problem (with a given s -wave scattering length) by a boundary-value problem.

ACKNOWLEDGMENTS

The author is pleased to thank Professor Morrel H. Cohen of the Institute for the Study of Metals for discussions which provided the stimulus for the present work.