PHYSICAL REVIEW VOLUME 184, NUMBER 1 5 AUGUST 1969

Quantum-Mechanical Equation of State of a Hard-Sphere Gas at High Temperature. II*

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(Received 16 January 1969)

As the continuation of a preceding paper, an expansion for the quantum-mechanical free energy F of a hard-sphere gas at high temperature is extended up to the second order in the thermal wavelength $\lambda=(2\pi\hbar^2/mkT)^{1/2}$. To reach this order, one must study the three-body problem in a lowest-order approximation, in which adjacent sphere surfaces can be regarded as parallel planes. Coefficients of the λ series for F are given in terms of classical correlation functions. Using known density expansions for these correlation functions, one can obtain λ expansions for the virial coefficients; the third virial coefficient is

$$B_3=(5\pi^2a^6/18)[1+(3/\sqrt{2})(\lambda/a)+1.707\,660\,(\lambda/a)^2+\cdots],$$

where a is the hard-sphere diameter (only the last term is a new result).

I. INTRODUCTION

In a previous paper,[1] the quantum-mechanical free energy of a hard-sphere gas at high temperature was studied as a series in powers of the thermal wavelength $\lambda=(2\pi\hbar^2/mk_BT)^{1/2}$ ($\hbar$ is Planck's constant divided by 2π, m is the mass of a sphere, k_B is Boltzmann's constant, T is the absolute temperature). Only the first-order term in λ was, however, explicitly given in sole terms of the classical thermodynamic quantities and correlation functions. The purpose of the present paper is to give an explicit expression for the second-order term in λ. At the same time, the third virial coefficient will be obtained as a series in λ up to the second-order term.[2]

In I, an expression for the quantum-mechanical free energy F, valid up to the second order in λ, was found to be

$$\frac{F}{Nk_BT}=\frac{F^{(0)}}{Nk_BT}-\rho c_2+\rho^2(2c_2{}^2-c_3)-\rho^3 f. \quad (1)$$

$F^{(0)}$ is the classical value of the free energy. N is the total number of particles. ρ is the number density N/Ω (Ω is the total volume of the system). The quantities c_l and f are defined as

$$c_l=(\Omega l!)^{-1}\int g_l(\vec{r}_1,\ldots,\vec{r}_l)\times U_l(\vec{r}_1,\ldots,\vec{r}_l)\,d\vec{r}_1\cdots d\vec{r}_l, \quad (2)$$

and

$$f=(8\Omega)^{-1}\int[g_4(\vec{r}_1,\vec{r}_2,\vec{r}_3,\vec{r}_4)-g_2(\vec{r}_1,\vec{r}_2)g_2(\vec{r}_3,\vec{r}_4)]\,U_2(\vec{r}_1,\vec{r}_2)\times U_2(\vec{r}_3,\vec{r}_4)\,d\vec{r}_1d\vec{r}_2d\vec{r}_3d\vec{r}_4, \quad (3)$$

where g_l is the l-body classical correlation function and U_l the quantum-mechanical l-body Ursell function.[3] U_2 is sufficiently well known.[4] The main task of the present paper will be to study U_3.

In order to derive from (1) an explicit expansion of F in powers of λ, up to the second order, we shall give sufficient simpler approximate expressions of c_2, c_3, and f, in Sec. II. The expression of c_3 involves an integral upon U_3, which can in turn be expressed in terms of the spatial distribution function W_3 for a three-body system; this function W_3 will be obtained in Sec. III, in the lowest approximation which is here sufficient. The resulting Ursell function U_3 will be integrated in Sec. IV, and the final result for the free energy will be obtained. The special case of the third virial coefficient will be considered in Sec. V.

II. CALCULATION OF c_2, c_3, AND f, UP TO THE ORDER λ^2

In (1), c_2, c_3, and f must be expanded up to the second order in λ. Exchange effects are exponentially small at high temperature, and do not contribute to power series in λ; they can be neglected in the computation of the Ursell functions U_l.

Since $g_2(\vec{r}_1,\vec{r}_2)$ and $U_2(\vec{r}_1,\vec{r}_2)$ actually only depend on the distance $r=|\vec{r}_2-\vec{r}_1|$, one has

$$c_2=2\pi\int_a^\infty g_2(r)U_2(r)r^2\,dr \quad (4)$$

[the lower bound of the integral has been taken as the hard-sphere diameter a, since $g_2(r)$ vanishes for smaller values of r]. Furthermore, since $U_2(r)$ has a range of order λ beyond a, c_2 can be written, up to the second order in λ, as

$$c_2 = 2\pi g_2(a) \int_a^\infty U_2(r) r^2\, dr + 2\pi g_2'(a) a^2 \int_a^\infty U_2(r)(r-a)\, dr\,. \tag{5}$$

The first term in (5) involves the quantum part of the second virial coefficient, which has been previously studied[4]:

$$-2\pi \int_a^\infty U_2(r)\, r^2\, dr = (\pi/\sqrt{2})\, a^2\lambda + \tfrac{2}{3} a\lambda^2 + \cdots\,. \tag{6}$$

The second term in (5) is of order λ^2, and can be computed within this order from the lowest-order approximation for $U_2(r)$:

$$U_2(r) \approx -\exp[-2\pi(r-a)^2/\lambda^2]\,, \quad r > a\,. \tag{7}$$

Therefore one finds

$$c_2 = -g_2(a)[(\pi/\sqrt{2})\, a^2\lambda + \tfrac{2}{3} a\lambda^2] - \tfrac{1}{2} g_2'(a) a^2\lambda^2 + \cdots\,. \tag{8}$$

For the calculation of c_3, it is convenient to take as the relative variables, describing a configuration of the spheres,

$$r_{13} = |\vec{r}_3 - \vec{r}_1|\,, \quad r_{23} = |\vec{r}_3 - \vec{r}_2|\,,$$

and the angle α between $\vec{r}_{13}$ and $\vec{r}_{23}$. One has

$$c_3 = \tfrac{4}{3}\pi^2 \int g_3(r_{13}, r_{23}, \alpha) U_3(r_{13}, r_{23}, \alpha) \times r_{13}{}^2\, dr_{13}\, r_{23}{}^2\, dr_{23}\, d(\cos\alpha)\,. \tag{9}$$

The leading contribution to c_3, which is of order λ^2, comes from cluster configurations such as the one depicted in Fig. 1: One of the spheres is almost at contact with both the other spheres.

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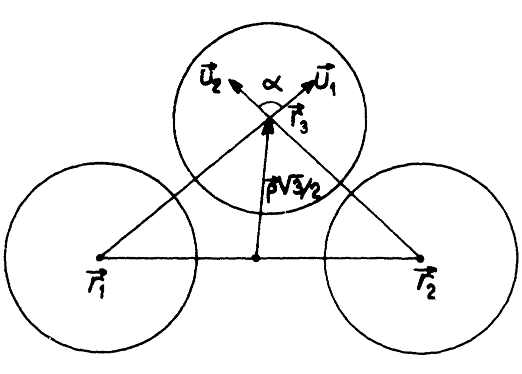

FIG. 1. A cluster configuration of three spheres.

The middle sphere can be chosen in three different ways. Therefore within the order λ^2,

$$c_3 = 4\pi^2 a^4 \int_{-1}^{1/2} d(\cos\alpha) g_3(a, a, \alpha) \times \int_a^\infty dr_{13} \int_a^\infty dr_{23}\, U_3(r_{13}, r_{23}, \alpha)\,. \tag{10}$$

Equation (10) involves an integral upon U_3, which will be computed in Sec. IV.

Finally, f is of order λ^2, and can be written within that order

$$f = (\lambda^2/64) \int [g_4(\vec{r}_1, \vec{r}_2, \vec{r}_3, \vec{r}_4) - g_2(\vec{r}_1, \vec{r}_2) g_2(\vec{r}_3, \vec{r}_4)] \times \delta(r_{12} - a)\delta(r_{34} - a)\, d\vec{r}_2\, d\vec{r}_3\, d\vec{r}_4\,, \tag{11}$$

where we have used (7) for computing

$$\int_a^\infty U_2(r)\, dr = -\lambda/2\sqrt{2} + \cdots\,. \tag{12}$$

III. THE SPATIAL DISTRIBUTION FUNCTION OF A THREE-SPHERE SYSTEM

A more explicit evaluation of c_3 from (10) requires some knowledge about U_3, the definition of which is

$$U_3(\vec{r}_1, \vec{r}_2, \vec{r}_3) = W_3(\vec{r}_1, \vec{r}_2, \vec{r}_3) - 1 - U_2(\vec{r}_1, \vec{r}_2) - U_2(\vec{r}_2, \vec{r}_3) - U_2(\vec{r}_3, \vec{r}_1), \tag{13}$$

where W_3 is the quantum-mechanical spatial distribution function for a system of three spheres, normalized in such a way that $W_3 = 1$ when these spheres are all far away from one another. We shall therefore proceed to the study of W_3.

This distribution function is given by

$$W_3 = C \sum_i e^{-E_i/k_B T}\, |\psi_i(\vec{r}_1, \vec{r}_2, \vec{r}_3)|^2, \tag{14}$$

where the summation runs on the complete set of the relative eigenfunctions ψ_i of the three-sphere system; E_i is the eigenvalue which is associated with ψ_i, and C is a normalization constant.

The total kinetic-energy operator, when expressed in terms of the variables

$$\vec{R} = (\vec{r}_1 + \vec{r}_2 + \vec{r}_3)/3\,, \quad \vec{r}_{12} = \vec{r}_2 - \vec{r}_1\,, \quad \vec{\rho} = (2\vec{r}_3 - \vec{r}_1 - \vec{r}_2)/\sqrt{3} \tag{15}$$

is

$$K = -(\hbar^2/6m)\,\Delta_{\vec{R}} - (\hbar^2/m)(\Delta_{\vec{r}_{12}} + \Delta_{\vec{\rho}})\,. \tag{16}$$

Therefore the relative eigenfunctions ψ_i and eigenvalues E_i are given by the Schrödinger equation

$$-(\hbar^2/m)(\Delta_{\vec{r}_{12}} + \Delta_{\vec{\rho}})\psi_i = E_i\psi_i \ , \qquad (17)$$

with the boundary conditions that ψ_i vanishes at

$$r_{12} = a, \quad \text{and} \quad |\vec{\rho}\sqrt{3}/2 \pm \vec{r}_{12}/2| = a \ . \qquad (18)$$

We are interested in cluster configurations like the one in Fig. 1. The distance between the surfaces of the spheres 1 and 2 is large compared to λ, and therefore the boundary condition at $r_{12} = a$ can be disregarded [the special case, in which all the three spheres are almost at contact of one another, would contribute to (9) only at the order λ^3, and has not to be taken into account here]. Furthermore, in the high-temperature limit ($\lambda/a \to 0$), the curvature effects disappear, and the sphere surfaces which are in front of one another can be regarded as parallel planes. Let $\vec{u}_1$ and $\vec{u}_2$ be the unit vectors parallel to $\vec{r}_3 - \vec{r}_1$ and $\vec{r}_3 - \vec{r}_2$, respectively, for some definite configuration (C). When the curvature effects are neglected, the problem is now to find the solution ψ_i of (17), defined for general values of $\vec{\rho}$ and $\vec{r}_{12}$, with the simplified boundary conditions that ψ_i vanishes on the flat manifolds

$$(\vec{\rho}\sqrt{3}/2 + \vec{r}_{12}/2) \cdot \vec{u}_1 = a,$$
$$\text{and} \quad (\vec{\rho}\sqrt{3}/2 - \vec{r}_{12}/2) \cdot \vec{u}_2 = a \ . \qquad (19)$$

In (19), $\vec{\rho}$ and $\vec{r}_{12}$ must be regarded as variables $\vec{u}_1$ and $\vec{u}_2$ as fixed parameters. These solutions ψ_i must then be used to compute W_3 through (14) for that configuration (C) which had been chosen for defining $\vec{u}_1$ and $\vec{u}_2$.

The components of $\vec{\rho}$ and $\vec{r}_{12}$ perpendicular to the $(\vec{u}_1, \vec{u}_2)$ plane are not involved in the boundary conditions (19); the dependence of ψ_i on these components will only contribute a constant factor to W_3. We will therefore only consider the motions in the $(\vec{u}_1, \vec{u}_2)$ plane. Let the Cartesian components in this plane be (ξ, η) for $\vec{\rho}$, (x, y) for $\vec{r}_{12}$, (μ_1, ν_1) for $\vec{u}_1$, (μ_2, ν_2) for $\vec{u}_2$. From (17), we see that W_3 is the spatial distribution function for a free particle of mass $m/2$ in the four-dimensional space spanned by (ξ, η, x, y), with the boundary conditions that the wave functions must vanish on two three-dimensional hyperplanes which are, from (19),

$$\xi\mu_1\sqrt{3}/2 + x\mu_1/2 + \eta\nu_1\sqrt{3}/2 + y\nu_1/2 = a$$
$$\text{and} \qquad (20)$$
$$\xi\mu_2\sqrt{3}/2 - x\mu_2/2 + \eta\nu_2\sqrt{3}/2 - y\nu_2/2 = a \ .$$

The unit four-vectors normal to these hyperplanes are

$$(\mu_1\sqrt{3}/2, \mu_1/2, \nu_1\sqrt{3}/2, \nu_1/2)$$
$$\text{and} \quad (\mu_2\sqrt{3}/2, -\mu_2/2, \nu_2\sqrt{3}/2, -\nu_2/2),$$

and the angle β between these four-vectors is defined by

$$\cos\beta = \tfrac{1}{2}(\mu_1\mu_2 + \nu_1\nu_2) = \tfrac{1}{2}\cos\alpha \ . \qquad (21)$$

The distances of the point (ξ, η, x, y) to the hyperplanes are

$$\xi\mu_1\sqrt{3}/2 + x\mu_1/2 + \eta\nu_1\sqrt{3}/2 + y\nu_1/2 - a = \vec{r}_{13} \cdot \vec{u}_1 - a$$
$$\text{and} \qquad (22)$$
$$\xi\mu_2\sqrt{3}/2 - x\mu_2/2 + \eta\nu_2\sqrt{3}/2 - y\nu_2/2 - a = \vec{r}_{23} \cdot \vec{u}_2 - a \ ;$$

for the configuration (C), these distances are $r_{13} - a$ and $r_{23} - a$.

Since W_3 depends only on these distances for a given β, the computation of W_3 can be made in any two-dimensional plane orthogonal to the hyperplanes (20). Therefore we finally have the following very simple result: In the high-temperature limit ($\lambda/a \to 0$), $W_3(r_{13}, r_{23}, \alpha)$ is proportional to the probability distribution of one particle of mass $m/2$, moving in a plane wedge (Fig. 2), the summit angle of which is $\theta = \pi - \beta$, where β is defined by (21); $r_{13} - a$ and $r_{23} - a$ are the distances of the particle to the edges, on which the wave functions are constrained to vanish.

In terms of polar coordinates (r, φ) chosen as in Fig. 2, the wave functions in the wedge are

$$\psi_i = \psi_{nk}$$
$$= (2k\pi/\theta R)^{1/2} J_{n\pi/\theta}(kr) \sin(n\pi\varphi/\theta) \ , \qquad (23)$$

where the quantum number n assumes integer positive values. In (23) ψ_{nk} has been normalized to

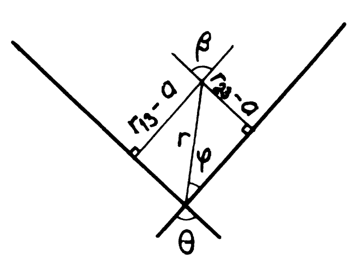

FIG. 2. One particle in a plane wedge.

1 in a circular sector of large radius R, as can be seen by using for the Bessel function J its asymptotic form[5] for large r values, since then

$$\psi_{nk} \sim [2/(\theta R r)^{1/2}] \cos(kr - n\pi^2/2\theta - \pi/4) \times \sin(n\pi\varphi/\theta). \quad (24)$$

The possible values of the wave number k are such that kR varies by integer multiples of π, and we obtain from (14) using a tabulated integral,[5]

$$W_3 = C \sum_{n=1}^{\infty} \frac{R}{\pi} \int_0^\infty dk \exp\left(\frac{-\hbar^2 k^2}{mk_B T}\right) |\psi_{nk}|^2$$
$$= C \frac{2}{\theta} \sum_{n=1}^{\infty} \int_0^\infty dk\, k \exp\left(\frac{-\lambda^2 k^2}{2\pi}\right) \times [J_{n\pi/\theta}(kr)]^2 \sin^2(n\pi\varphi/\theta)$$
$$= C \frac{2\pi}{\theta\lambda^2} \sum_{n=1}^{\infty} \exp\left(\frac{-\pi r^2}{\lambda^2}\right) \times I_{n\pi/\theta}(\pi r^2/\lambda^2) \sin^2(n\pi\varphi/\theta), \quad (25)$$

where I is a Bessel function of imaginary argument. In order to find the normalization constant C, we note that, far from the edges, the result $W_3 = 1$ must be obtained from a Cartesian-coordinate evaluation:

$$1 = \frac{C}{(2\pi)^2} \int dk_x dk_y \exp\left(\frac{-\hbar^2(k_x^2 + k_y^2)}{mk_B T}\right) = C/2\lambda^2. \quad (26)$$

Therefore

$$W_3 = \frac{4\pi}{\theta} \sum_{n=1}^{\infty} \exp\left(\frac{-\pi r^2}{\lambda^2}\right) \times I_{n\pi/\theta}(\pi r^2/\lambda^2) \sin^2(n\pi\varphi/\theta). \quad (27)$$

IV. INTEGRATION UPON THE THREE-BODY URSELL FUNCTION. FINAL RESULT FOR THE FREE ENERGY

In lowest approximation, U_3 can be obtained from (13) with the use of (7) and (27), and with the neglect of $U_2(\vec{r}_1, \vec{r}_2)$ for those configurations we are interested in. We have to compute, for its further use in (10)

$$A(\alpha) = \int_a^\infty dr_{13} \int_a^\infty dr_{23}\, U_3(r_{13}, r_{23}, \alpha)$$
$$= \int_a^\infty dr_{13} \int_a^\infty dr_{23} [W_3 - 1 - U_2(r_{13}) - U_2(r_{23})]. \quad (28)$$

It is convenient to introduce $\exp(-\epsilon^2 r^2)$ as a con vergence factor; it is then possible to compute separately the contributions of W_3, 1 and each U to (28):

$$A = \lim_{\epsilon \to 0} [A_3 + A_1 + 2A_2]. \quad (2$$

For A_3, one has

$$A_3 = \int_a^\infty dr_{13} \int_a^\infty dr_{23} e^{-\epsilon^2 r^2} W_3$$
$$= \sin\theta \int_0^\infty dr\, r \int_0^\theta d\varphi \frac{4\pi}{\theta} \sum_{n=1}^{\infty} e^{-(\epsilon^2 + \pi/\lambda^2) r} \times I_{n\pi/\theta}(\pi r \ \ /\lambda^2) \sin^2(n\pi\varphi/\theta). \quad (3$$

The integrals in (30) can be explicitly evaluated One obtains a geometric series, the sum of whi can be expanded for small ϵ values, with the re sult

$$A_3 = \sin\theta[\theta/2\epsilon^2 - \lambda(\tfrac{1}{2}\pi)^{1/2}/2\epsilon - \lambda^2\theta/12\pi + \lambda^2\pi/12\theta + O(\epsilon)]. \quad (31$$

The evaluation of A_1 and A_2 is straightforward:

$$A_1 = -\int_a^\infty dr_{13} \int_a^\infty dr_{23} e^{-\epsilon^2 r^2}$$
$$= -\sin\theta \int_0^\theta d\varphi \int_0^\infty dr\, r\, e^{-\epsilon^2 r^2}$$
$$= -\sin\theta(\theta/2\epsilon^2), \quad (3$$
$$A_2 = -\int_a^\infty dr_{13} \int_a^\infty dr_{23} e^{-\epsilon^2 r^2} U_2(r_{23})$$
$$= \sin\theta \int_0^\theta d\varphi \int_0^\infty dr\, r \times \exp[-(\epsilon^2 + 2\pi \sin^2\varphi/\lambda^2) r^2]$$
$$= \sin\theta[\lambda(\tfrac{1}{2}\pi)^{1/2}/4\epsilon - (\lambda^2/4\pi)\cot\theta + O(\epsilon)]. \quad (3$$

When all contributions to (28) are put together, gets

$$A = \lambda^2 \left[\left(\frac{\pi}{12\theta} - \frac{\theta}{12\pi}\right) \sin\theta - \frac{1}{2\pi}\cos\theta\right]. \quad (3$$

When

$$\theta = \pi - \cos^{-1}(\tfrac{1}{2}\cos\alpha)$$

is used as the angular integration variable in (1 one finds

$$c_3 = \pi^2 a^4 \lambda^2 \int_{\pi/3}^{\cos^{-1}(-1/4)} g_3(a, a, \alpha)$$

$$\times \left[\left(\frac{2\pi}{3\theta} - \frac{2\theta}{3\pi} \right) \sin\theta - \frac{4}{\pi} \cos\theta \right] \sin\theta \, d\theta \, . \tag{35}$$

At this point, we have completed the evaluation of the quantum-mechanical free energy F in terms of classical quantities. Up to the second order in λ, the result is expressed by (1), where c_2 is given by (8), f by (11), and c_3 by (35). The free energy depends upon the density not only through the explicit ρ factors in (1), but also because the correlation functions, in c_2, f, and c_3, are density-dependent. The pressure can be computed in principle by differentiating F with respect to ρ.

V. THE THIRD VIRIAL COEFFICIENT

The virial coefficients can be obtained through an expansion of (1) with respect to ρ. The ρ expansion of c_2 is obtained by using in (8) the ρ expansion of the two-body correlation function[6]

$$g_2(r) = 1 + \rho \tfrac{2}{3}\pi a^3 [2 - 3r/2a + r^3/8a^3] + \cdots \, , \quad a \leq r \leq 2a, \tag{36}$$

with the result

$$c_2 = -\frac{\pi a^2 \lambda}{\sqrt{2}} + \frac{2a\lambda^2}{3} + \rho \left(\frac{-5\pi^2 a^5 \lambda}{12\sqrt{2}} + \frac{7\pi a^4 \lambda^2}{72} \right) + \cdots \, . \tag{37}$$

For obtaining the free energy up to its second-order term in ρ, it is enough to use in (1) the ρ-independent part of c_3, which will be obtained in turn by taking in (35) the leading term of the three-body correlation function, $g_3(a, a, \alpha) = 1$, for $\pi/3 \leq \alpha \leq \pi$:

$$c_3 = \pi^2 a^4 \lambda^2 \int_{\pi/3}^{\cos^{-1}(-1/4)} \left[\left(\frac{2\pi}{3\theta} - \frac{2\theta}{3\pi} \right) \sin\theta - \frac{4}{\pi} \cos\theta \right] \sin\theta \, d\theta + \cdots$$

$$= 0.721\,878\,2 \pi^2 a^4 \lambda^2 + \cdots \equiv \tau \pi^2 a^4 \lambda^2 + \cdots \, . \tag{38}$$

Finally, f does not contribute to F up to the order ρ^2. One finds for the free energy (1) a ρ expansion from which the ρ expansion of the pressure is readily obtained

$$\frac{p}{\rho k_B T} = \rho \frac{\partial}{\partial \rho} \frac{F}{N k_B T} = 1 + B_2 \rho + B_3 \rho^2 + \cdots \, . \tag{39}$$

In the classical limit, B_2 and B_3 are well known.[7] Adding our quantum corrections, we find for the second virial coefficient

$$B_2 = \tfrac{2}{3}\pi a^3 \left[1 + \frac{3}{2\sqrt{2}} \frac{\lambda}{a} + \frac{1}{\pi} \left(\frac{\lambda}{a} \right)^2 + \cdots \right] , \tag{40}$$

a result which was already known,[4] and for the third virial coefficient

$$B_3 = \tfrac{5}{18}\pi^2 a^6 \left[1 + \frac{3}{\sqrt{2}} \frac{\lambda}{a} + \left(\frac{-7}{10\pi} + \frac{36}{5} - \frac{36\tau}{5} \right) \left(\frac{\lambda}{a} \right)^2 + \cdots \right]$$

$$= \tfrac{5}{18}\pi^2 a^6 \left[1 + \frac{3}{\sqrt{2}} \frac{\lambda}{a} + 1.707\,660 \left(\frac{\lambda}{a} \right)^2 + \cdots \right] \tag{41}$$

(the first-order term in λ was already known[1,8]).

VI. ACKNOWLEDGMENTS

Part of this work was done at Yeshiva University; the author is indebted to Professor J. L. Lebowitz for both his kind hospitality and his stimulating interest.

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*Work supported in part by the U. S. Air Force under Grant No. AF68-1416.

†Laboratoire associé au Centre National de la Recherche Scientifique.

[1]B. Jancovici, Phys. Rev. 178, 295 (1969), hereafter referred to as I.

[2]This high-temperature expansion should not be confused with the low-temperature one: G. E. Uhlenbeck and A. Pais, Phys. Rev. 116, 250 (1959).

[3]B. Kahn, Ph. D. dissertation, University of Utrecht, 1938, reprinted in Studies in Statistical Mechanics, edited by J. de Boer and G. E. Uhlenbeck (North-Holland Publishing Co., Amsterdam, 1965), Vol. III, p. 277.

[4]R. A. Handelsman and J. B. Keller, Phys. Rev. 148, 94 (1966); P. C. Hemmer and K. J. Mork, *ibid.* 158, 114 (1967); R. N. Hill, J. Math. Phys., 9, 1534 (1968).

[5]I. S. Gradshteyn and I. M. Ryzhik, Table of Integrals, Series, and Products, translation edited by A. Jeffrey (Academic Press Inc., New York, 1965).

[6]J. G. Kirkwood, J. Chem. Phys. 3, 300 (1935).

[7]F. H. Ree and W. G. Hoover, J. Chem. Phys. 46, 4181 (1967), and references quoted there.

[8]P. C. Hemmer, Phys. Letters, 27A, 377 (1968).