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

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The quantum-mechanical free energy F of a hard-sphere gas at high temperature is a series in powers of the thermal wavelength $\lambda = (2\pi\hbar^2/mkT)^{1/2}$; the coefficients of this series can be expressed in terms of the classical correlation functions. The result to first order is

$$\frac{F}{NkT} = \frac{F^{(0)}}{NkT} + \frac{\pi}{\sqrt{2}}\, g_2(a) a^2 \rho \lambda,$$

where $F^{(0)}$ is the classical free energy, N the total number of particles, ρ the number density, kT Boltzmann's factor times the temperature, a the hard-sphere diameter, $g_2(a)$ the classical pair-correlation function at contact. The corresponding expression for the pressure is

$$p = p^{(0)} + \frac{3}{2\sqrt{2}} \frac{\lambda}{a} \rho^2 \frac{\partial}{\partial \rho} \frac{p^{(0)}}{\rho}$$

where $p^{(0)}$ is the classical pressure. The principle of a systematic derivation of higher-order terms in λ is given.

At high temperature, the quantum effects in the equation of state of a gas are small and appear as corrections. In the special case of a hard-sphere gas, these corrections cannot be obtained by Wigner and Kirkwood's expansion[1] in powers of $\hbar^2$, the terms of which diverge ($\hbar$ is Planck's constant divided by 2π). An expansion in powers of $\hbar$ may, however, exist and will be described in the present paper. The classical thermodynamic quantities and correlation functions are assumed to be known, and we wish to express the quantum corrections in terms of these classical quantities.

As a first hint, since the wave functions vanish when two spheres contact, we may expect that the sphere surfaces will keep away from one another by a distance of the order of the thermal wave length $\lambda = (2\pi\hbar^2/mkT)^{1/2}$ (m is the mass of a sphere, k is Boltzmann's constant, T is the absolute temperature). Quantum effects therefore can be taken into account in a first approximation through an increase of the hard-sphere diameter a by a quantity of the order of λ. It will be shown more precisely that first-order quantum effects amount to the replacement of a by $a + (\lambda/2\sqrt{2})$. In classical mechanics, the pressure $p^{(0)}$ is of the form

$$p^{(0)} = kT\rho f(\rho a^3), \tag{1}$$

where ρ is the number density and f some function. The quantum expression p for the pressure is given to first order as

$$p = p^{(0)} + \frac{\partial p^{(0)}}{\partial a} \frac{\lambda}{2\sqrt{2}} = p^{(0)} + \frac{3}{2\sqrt{2}} \frac{\lambda}{a} \rho^2 \frac{\partial}{\partial \rho} \frac{p^{(0)}}{\rho}\ . \tag{2}$$

A systematic expansion of the free energy in powers of λ can be obtained as follows. We consider N hard spheres in a volume Ω. Let $W(\vec{r}_1, \ldots, \vec{r}_N)$ be the quantum-mechanical total spatial distribution function.[2] W is normalized in such a way that $W = 1$ when all spheres are far away from one another; W goes continuously to zero as two spheres approach one another, and vanishes when two spheres intersect. Let $W^{(0)}(\vec{r}_1, \ldots, \vec{r}_N)$ be the classical limit of W. Since $W^{(0)} = 0$ when W vanishes and $W^{(0)} = 1$ when W does not vanish, one has

$$W = W^{(0)} W\,, \tag{3}$$

a fundamental relation which allows us at will to use $W^{(0)}$ as a weight function when we perform any integration upon W.

Now W can be expanded as a sum of products of Ursell functions U_l:

$$W(\vec{r}_1, \ldots, \vec{r}_N) = 1 + U_2(\vec{r}_1, \vec{r}_2) + \cdots + U_3(\vec{r}_1, \vec{r}_2, \vec{r}_3) + \cdots + U_4(\vec{r}_1, \vec{r}_2, \vec{r}_3, \vec{r}_4) + \cdots + U_2(\vec{r}_1, \vec{r}_2) U_2(\vec{r}_3, \vec{r}_4) + \cdots\,. \tag{4}$$

Each term in (4) corresponds to one of the possible partitions of the N particles in clusters; a cluster of l particles contributes a factor U_l, and we have used the fact that $U_1 = 1$. The Ursell functions are defined as usual from the set of the W functions for different values of N through the relations

$$W(\vec{r}_1)=U_1(\vec{r}_1)=1,\quad W(\vec{r}_1,\vec{r}_2)=U_1(\vec{r}_1)U_1(\vec{r}_2)+U_2(\vec{r}_1,\vec{r}_2),\ \text{etc.}\tag{5}$$

U_l has the cluster property that it goes to zero as soon as the surface-to-surface distance between one sphere it refers to and all the other ones is large compared to λ.

We now proceed to the computation of the configuration integral $Q=\int W(\vec{r}_1,\ldots,\vec{r}_N)d\vec{r}_1\cdots d\vec{r}_N$. Let $Q^{(0)}$ be the classical limit of Q, and let

$$g_l(\vec{r}_1,\ldots,\vec{r}_l)=\Omega^l\int W^{(0)}(\vec{r}_1,\ldots,\vec{r}_N)d\vec{r}_{l+1}\cdots d\vec{r}_N/Q^{(0)}\tag{6}$$

be the classical l-body correlation function. One gets from (3), (4), and (6)

$$Q=Q^{(0)}\Big(1+\frac{1}{\Omega^2}\int g_2(\vec{r}_1,\vec{r}_2)U_2(\vec{r}_1,\vec{r}_2)d\vec{r}_1d\vec{r}_2+\cdots+\frac{1}{\Omega^3}\int g_3(\vec{r}_1,\vec{r}_2,\vec{r}_3)U_3(\vec{r}_1,\vec{r}_2,\vec{r}_3)d\vec{r}_1d\vec{r}_2d\vec{r}_3+\cdots$$
$$+\frac{1}{\Omega^4}\int g_4(\vec{r}_1,\vec{r}_2,\vec{r}_3,\vec{r}_4)[U_4(\vec{r}_1,\vec{r}_2,\vec{r}_3,\vec{r}_4)+U_2(\vec{r}_1,\vec{r}_2)U_2(\vec{r}_3,\vec{r}_4)+\cdots]d\vec{r}_1d\vec{r}_2d\vec{r}_3d\vec{r}_4\Big)+\cdots.\tag{7}$$

As a consequence of the cluster property of the U_l functions, a term $U_lU_m\cdots U_n$ in (4) contributes to (7) an integral of order $\lambda^{l-1+m-1+\cdots+n-1}$, and (4) can be truncated in a well-defined way, if one is interested only in terms up to a given order in λ. In addition to these powers of λ, there will be terms like $\exp[-c(a/\lambda)^2]$ which will be generated by the exchange parts[3] of the U_l functions; such terms are negligible, but their presence shows that one may hope at best to obtain asymptotic series.

To first order in λ, it is enough to keep in (4) the $N(N-1)/2$ terms U_2, and therefore

$$Q\approx Q^{(0)}[1+N(N-1)c_2/\Omega],\tag{8}$$

where $c_2=(1/2\Omega)\int g_2(\vec{r}_1,\vec{r}_2)U_2(\vec{r}_1,\vec{r}_2)d\vec{r}_1d\vec{r}_2$; (9)

c_2 is of order λ. Taking the logarithms in (8) and expanding with respect to λ, one finds for the free energy F the classical value $F^{(0)}$ plus a correction of order λ as follows:

$$F/NkT=F^{(0)}/NkT-(1/N)\ln(Q/Q^{(0)})\approx F^{(0)}/NkT-\rho c_2,\tag{10}$$

where $(N-1)/\Omega\approx N/\Omega=\rho$. It is enough to take for U_2 the zeroth-order term[4] in an expansion in powers of λ/a:

$$U_2(\vec{r}_1,\vec{r}_2)=-\exp\{-[2\pi(r-a)^2/\lambda^2]\},\quad r>a,\tag{11}$$

where $r=|\vec{r}_1-\vec{r}_2|$. Incidentally, U_2 has a "quantum range" beyond a which is

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

and this provides a heuristic justification for the result (2). In the present derivation, we use (11) in (9) and obtain

$$c_2\approx\tfrac{1}{2}g_2(a)4\pi a^2\int_a^\infty U_2(r)=-(\pi/\sqrt{2})g_2(a)a^2\lambda\tag{13}$$

and, from (10),

$$F/NkT=F^{(0)}/NkT+(\pi/\sqrt{2})g_2(a)a^2\rho\lambda\ .\tag{14}$$

The pressure can be obtained from the free energy (14) by taking the derivative

$$p=\rho^2\frac{\partial}{\partial\rho}\frac{F}{N}\,.\tag{15}$$

If one expresses $g_2(a)$ in (14) in terms of the classical pressure $p^{(0)}$ through the well-known expression

$$p^{(0)}/kT=\rho+\tfrac{2}{3}\pi g_2(a)a^3\rho^2,\tag{16}$$

one recovers (2). The virial expansion of (2)

$$\frac{p}{kT}=\rho+\sum_{l\geqslant 2}B_l\rho^l\tag{17}$$

provides the corrections of first order in λ to all the virial coefficients:

$$B_l=B_l^{(0)}[1+(l-1)(3/2\sqrt{2})\lambda/a]\,.\tag{18}$$

Higher-order terms in λ for the free energy could in principle be obtained in a similar way, but one should first compute U_l functions for higher values of l and to higher orders in λ/a. Consider for instance the second-order term in λ. We must keep in (4) not only the $N(N-1)/2$ terms U_2, but also the $N(N-1) \times (N-2)/6$ terms U_3 and the $N(N-1)(N-2)(N-3)/8$ terms U_2U_2. Therefore,

$$Q \approx Q^{(0)}\left(1+\frac{N(N-1)}{\Omega}c_2+\frac{N(N-1)(N-2)}{\Omega^2}c_3+\frac{N(N-1)(N-2)(N-3)}{\Omega^3}d\right), \tag{19}$$

where $c_l = (\Omega l!)^{-1}\int g_l(\vec{r}_1,\ldots,\vec{r}_l)U_l(\vec{r}_1,\ldots,\vec{r}_l)d\vec{r}_1\cdots d\vec{r}_l\,,$ (20)

and $d=(8\Omega)^{-1}\int g_4(\vec{r}_1,\ldots,\vec{r}_4)U_2(\vec{r}_1,\vec{r}_2)U_2(\vec{r}_3,\vec{r}_4)d\vec{r}_1d\vec{r}_2d\vec{r}_3d\vec{r}_4\,.$ (21)

The free energy now is given by

$$\frac{F}{NkT}=\frac{F^{(0)}}{NkT}-\frac{1}{N}\ln\frac{Q}{Q^{(0)}}=\frac{F^{(0)}}{NkT}-\frac{N-1}{\Omega}c_2-\frac{(N-1)(N-2)}{\Omega^2}c_3-\frac{(N-1)(N-2)(N-3)}{\Omega^3}d+\frac{N(N-1)^2}{2\Omega^2}c_2{}^2+\cdots\,. \tag{22}$$

The integrals c_l are finite in the thermodynamic limit, but d is infinite. It is convenient to introduce the integral

$$f=d-\tfrac{1}{2}\Omega c_2{}^2=(1/8\Omega)\int[g_4(\vec{r}_1,\vec{r}_2,\vec{r}_3,\vec{r}_4)-g_2(\vec{r}_1,\vec{r}_2)g_2(\vec{r}_3,\vec{r}_4)]\,U_2(\vec{r}_1,\vec{r}_2)U_2(\vec{r}_3,\vec{r}_4)d\vec{r}_1d\vec{r}_2d\vec{r}_3d\vec{r}_4\,, \tag{23}$$

which is finite in the thermodynamic limit. Neglecting terms of order $1/N$, one finds from (22)

$$F/NkT=F^{(0)}/NkT-\rho c_2+\rho^2(2c_2{}^2-c_3)-\rho^3 f\,. \tag{24}$$

One should finally express the constants c_2, c_3, and f in (24) in terms of λ, up to the second order in λ. One needs an expression for U_2 valid beyond (11), i.e., to the next order in λ/a, which is available[5]; one would also need the leading term of U_3, which has not been computed. It should be noted, however, that one obtains for c_2, c_3 and f expressions involving the classical correlation functions g_l up to g_4, and such detailed information about the classical gas is not readily available anyhow.

As a conclusion, it might be noted that this property of the hard-sphere gas, namely, that the quantum corrections to the pressure involve a series in powers of $\hbar$ rather than $\hbar^2$, bears some similarity to the behavior of the classical velocity autocorrelation function, which is a power series in the time t rather than in t^2.

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