(1957).

[4] J. G. Dash and R. D. Taylor, Phys. Rev. 107, 1228 (1957).

[5] J. A. Tyson, Phys. Rev. 166, 166 (1968).

[6] Reference 3, Eq. (31).

[7] J. B. Mehl and W. Zimmermann, Phys. Rev. 167, 214 (1968).

[8] J. Goodwin and W. D. McCormick (unpublished).

[9] D. L. Elwell and H. Meyer, Phys. Rev. 164, 245 (1967); D. L. Elwee, Ph.D. thesis, Duke University, 1967 (unpublished). Vapor-pressure density data are given by E. C. Kerr and R. D. Taylor, Ann. Phys. (N.Y.) 26, 292 (1964).

[10] V. P. Peshkov and K. N. Zinoveva, Zh. Eksperim. i Teor. Fiz. 18, 438 (1948).

[11] R. D. Maurer and M. A. Herlin, Phys. Rev. 82, 329 (1951).

[12] O. V. Lounasmaa, Cryogenics 1, 212 (1961).

[13] C. J. N. Van den Meijdenberg *et al.*, Physica 27, 197 (1961).

[14] R. B. Dingle, Proc. Phys. Soc. (London) A63, 638 (1950). See also, F. London, Superfluids (John Wiley & Sons, Inc., New York, 1954), Vol. II, p. 85.

[15] Such a coupling has recently been observed directly: G. Jacucci and G. Signorelli, Phys. Letters 26A, 5 (1967); A. Hofmann, K. Keck, and G. U. Schubert, *ibid.* 26A, 598 (1968).

[16] Even at the vapor pressure, Eq. (4) is inadequate in studies of the critical region very near the λ point: C. J. Pearce, J. A. Lipa, and M. J. Buckingham, Phys. Rev. Letters 20, 1471 (1968); J. A. Tyson and D. H. Douglass, *ibid.* 21, 1308 (1968); D. L. Johnson and M. J. Crooks, *ibid.* 27A, 688 (1968).

[17] E. R. Grilly, Phys. Rev. 149, 97 (1966).

---

PHYSICAL REVIEW VOLUME 186, NUMBER 1 5 OCTOBER 1969

# Quantum Corrections to the Square-Well Classical Second Virial Coefficient

Trygve S. Nilsen

*Institutt for Teoretisk Fysikk, NTH,* 7034 *Trondheim, Norway*

(Received 1 April 1969)

The first quantum correction to the classical value of the second virial coefficient for the square-well potential is calculated. The result is $B(T)=\frac{2}{3}\pi d^3[\eta^3+(1-\eta^3)\,e^{-\beta u}]+2^{-1/2}\pi\lambda d^2\{e^{-\beta u}+\eta^2[1+e^{-\beta u}-2e^{-\beta u/2}I_0(\frac{1}{2}\beta u)]\}$, with $\lambda=(h^2/2\pi mkT)^{1/2}$ and $\beta=(kT)^{-1}$. Here, $u$ denotes the depth of the well, $d$ is the diameter of the hard core, and $\eta d$ is the range of the potential.

## I. INTRODUCTION

The purpose of this paper is to give the first quantum correction to the classical value of the second virial coefficient $B(T)$ for a gas of particles interacting via the square-well potential:

$$\begin{aligned}\psi(r)&=\infty, &&\text{for } r<d\\ &=u, &&\text{for } d<r<\eta d\\ &=0, &&\text{for } r<\eta d\end{aligned}\qquad(1)$$

where $u$ is a constant. This simple-model potential is supposed to represent the effect of a real intermolecular potential fairly well. To calculate the classical second virial coefficient for this potential is trivial.[1] For light gases, however, the quantum corrections are not completely negligible.[2]

The quantum-mechanical second virial coefficient for the square-well potential has two noteworthy features. First, it cannot be obtained by the usual Wigner-Kirkwood high-temperature expansion[3] because that expansion is essentially an expansion in powers of the gradient operator, and is therefore not applicable to the singular square-well potential.[4] Second, the presence of the hard core in the potential implies that at high temperatures all symmetrization effects are negligible or, more precisely, are exponentially small.[5] In a series expansion of $B(T)$ in powers of the ratio of the thermal deBroglie wavelength $\lambda=(h^2/2\pi mkT)^{1/2}$ to the hard-core diameter $d$, it therefore suffices to consider the spin-independent part $B_{\text{direct}}$.

## II. CALCULATIONS

The direct part of the second virial coefficient follows from the thermal Green's function by[6, 7]

$$B_{\text{dir}} = \tfrac{1}{2} \int d\vec{r}_0 [1 - 2\sqrt{3}\,\lambda^3 G(\vec{r}_0, \vec{r}_0; \beta)] \quad . \tag{2}$$

For the square-well potential, the Green's function satisfies

$$G(\vec{r}, \vec{r}_0; \beta) = 0, \quad \text{for } |\vec{r} - \vec{r}_c| \leq d \tag{3}$$

$$\left(\frac{\partial}{\partial\beta} - D\nabla^2 + u\right) G = 0, \quad \text{for } d < |\vec{r} - \vec{r}_c| < \eta d \tag{4}$$

$$\left(\frac{\partial}{\partial\beta} - D\nabla^2\right) G = 0, \quad \text{for } |\vec{r} - \vec{r}_c| > \eta d \tag{5}$$

with the initial condition

$$\lim_{\beta \to 0} G(\vec{r}, \vec{r}_0; \beta) = \delta(\vec{r} - \vec{r}_0) \quad . \tag{6}$$

here $D$ is related to the mass of a single molecule by $D = \hbar^2/m$, the point $\vec{r}_c$ is the center of the potential, and $\beta = (kT)^{-1}$. At the surface $|\vec{r} - \vec{r}_c| = \eta d$, both the function and its normal derivative have to be continuous.

To solve this "diffusion" problem completely is not easy.[2] But, for our purpose, a high-temperature expansion to the first order in $\lambda/d$, we may take advantage of the following simplifying features: (i) At distances $\gg\lambda$ from the boundaries, the quantum-mechanical corrections to the Green's function are negligible. This allows us to neglect the boundary at $|\vec{r} - \vec{r}_c| = \eta d$ when calculating the corrections due to the hard core and vice versa. In the one-dimensional case, the problem can be solved with and without this simplification, and the difference between the two results can be shown to be of the order $\exp[-d^2/\lambda^2]$, i.e., negligible to $O(\lambda/d)$; (ii) to lowest order in $\lambda/d$, the diameter of the sphere is infinite. Thus, the spherical boundaries appear planar to lowest order.

This means that we have reduced our problem of solving (3)–(5), simultaneously, to solving (3) and (4), or (4) and (5), separately, depending on which region we are interested in. And we can replace the boundary conditions on a sphere by boundary conditions on a plane.

Let us first consider the case when the source $\vec{r}_0 = (0, 0, z_0)$ is outside the well. It is then convenient to use coordinates such that the center of the sphere is at $(0, 0, -\eta d)$. Taking the Laplace transform of (4) and (5), with respect to $\beta$ and using (6), we get

$$sg - D\nabla^2 g + ug = 0 \ , \quad \text{for } z < 0 \tag{7}$$

$$sg - \delta(\vec{r} - \vec{r}_0) - D\nabla^2 g = 0 \ , \quad \text{for } z > 0. \tag{8}$$

Here, $g(\vec{r}, \vec{r}_0; s)$ is the Laplace transform of $G(\vec{r}, \vec{r}_0; \beta)$. As the solution of the diffusion equation $\partial G/\partial\beta - D\nabla^2 G = 0$ for diffusion from a unit point source in infinite space is

$$(4\pi D\beta)^{-3/2} \exp\{-[R^2 + (z - z_0)^2]/4DB\},$$

one particular solution of (8) is the Laplace transfor of this, namely,[8]

$$v = \frac{1}{4\pi D} \frac{\exp\{-[sD^{-1}]^{1/2}[R^2 + (z - z_0)^2]^{1/2}\}}{[R^2 + (z - z_0)^2]^{1/2}}, \tag{9}$$

$$v = \frac{1}{4\pi D} \int_0^\infty d\xi\, \xi J_0(\xi R)(\xi^2 + sD^{-1})^{-1/2}$$

$$\times \exp[-(\xi^2 + sD^{-1})^{1/2}\, |z - z_0|] \quad . \tag{10}$$

Here $R^2 = x^2 + y^2$ and $J_0$ is the Bessel function of first kind and zero order. The general solution of the corresponding homogeneous equation which, for $z > 0$, vanishes when $|\vec{r}| \to \infty$, is given by

$$w = \int_0^\infty d\xi\, A(\xi) J_0(\xi R) \exp[-(\xi^2 + sD^{-1})^{1/2} z] \quad . \tag{11}$$

The general solution of (8) is thus $g = v + w$. Likewise, the general solution of (7) is

$$g = \int_0^\infty d\xi\, B(\xi) J_0(\xi R) \exp[(\xi^2 + sD^{-1} + uD^{-1})^{1/2} z] \ . \tag{12}$$

Matching these solutions and their normal derivatives at $z = 0$ determines the unknown functions $A(\xi)$ and $B(\xi)$. For $z > 0$ (which is the only solution that we are interested in when $z_0 > 0$), we get

$$g = \frac{1}{4\pi D} \int_0^\infty d\xi\, \xi J_0(\xi R)(\xi^2 + sD^{-1})^{-1/2}$$

$$\times \{\exp[-(\xi^2 + sD^{-1})^{1/2} |z - z_0|]$$

$$+ \frac{(\xi^2 + sD^{-1})^{1/2} - (\xi^2 + sD^{-1} + uD^{-1})^{1/2}}{(\xi^2 + sD^{-1})^{1/2} + (\xi^2 + sD^{-1} + uD^{-1})^{1/2}}$$

$$\times \exp[-(\xi^2 + sD^{-1})^{1/2}(z + z_0)]\} \quad . \tag{13}$$

In the same manner, we can find the Laplace transform of the Green's function when the source is inside the well and close to the outer boundary,

$$g = \frac{1}{4\pi D} \int_0^\infty d\xi\, \xi J_0(\xi R)(\xi^2 + sD^{-1} + uD^{-1})^{-1/2}$$

$$\times \{\exp[-(\xi^2 + sD^{-1} + uD^{-1})^{1/2} |z - z_0|]$$

$$+\frac{(\xi^2+sD^{-1}+uD^{-1})^{1/2}-(\xi^2+sD^{-1})^{1/2}}{(\xi^2+sD^{-1}+uD^{-1})^{1/2}+(\xi^2+sD^{-1})^{1/2}}$$

$$\times\exp[-(\xi^2+sD^{-1}+uD^{-1})^{1/2}(z+z_0)]\}\,, \qquad (14)$$

and when it is close to the hard core

$$g=\frac{1}{4\pi D}\left(\frac{\exp\{-[(s+u)D^{-1}]^{1/2}[R^2+(z+z_0)^2]^{1/2}\}}{[R^2+(z-z_0)^2]^{1/2}}\right.$$

$$\left.-\frac{\exp\{-[(s+u)D^{-1}]^{1/2}[R^2+(z+z_0)^2]^{1/2}\}}{[R^2+(z+z_0)^2]^{1/2}}\right)\,. \qquad (15)$$

We have in Eq. (15) translated the coordinate system such that $\vec{r}_c=(0,0,-d)$ .

When these results are inserted into (2) it is a straightforward matter to perform the integration over $\vec{r}_0$ first, to invert the Laplace transform afterwards, and to do the integration over $\xi$ at the end. In the quantum-correction terms, the integration over the width of the well may be extended to infinity.

Also, in those terms, the factor $r_0^2$ in the volume element $d\vec{r}_0=4\pi r_0^2 dr_0$ is, to lowest order, constant, and is equal to $d^2$ or $(\eta d)^2$, respectively.

The result is

$$B(T)=\tfrac{2}{3}\pi d^3[\eta^3+(1-\eta^3)e^{-\beta u}]+2^{-1/2}\pi\lambda d^2$$

$$\times\{e^{-\beta u}+\eta^2[1+e^{-\beta u}-2e^{-\beta u/2}I_0(\tfrac{1}{2}\beta u)]\}\,, \qquad (16)$$

where $I_0$ is the modified Bessel function of first kind and order zero.[9] When one puts $u=0$ and $u=\infty$ in (16), the results check with those for hard spheres of diameter $d$ and $\eta d$, respectively.[10]

The first-order relative shift of the Boyle temperature $T_B$ is given by

$$(T_B-T_B^{cl})/T_B^{cl}=-(3/2\sqrt{2})\lambda/d$$

$$\times\frac{2\eta^2-\eta^{-1}+1-2\eta^2(1-\eta^{-3})^{1/2}I_0(\tfrac{1}{2}\ln(1-\eta^{-3}))}{(\eta^3-1)\ln(1-\eta^{-3})}\,. \qquad (17)$$

## ACKNOWLEDGMENTS

I should like to thank Professor P. C. Hemmer for introducing me to the problem. Stimulating discussions with him and with Dr. A. Theumann are gratefully acknowledged.

---

[*] Present address: Matematisk Institutt, Avd. B, Universitetet i Bergen, Bergen, Norway.

[1] J. O. Hirschfelder, C. F. Curtis, and R. B. Bird, Molecular Theory of Gases and Liquids (John Wiley & Sons, Inc., New York, 1954), p. 158.

[2] G. E. Uhlenbeck and E. Beth, Physica 3, 729 (1936); J. de Boer and A. Michels, *ibid.* 6, 409 (1939).

[3] E. Wigner, Phys. Rev. 40, 747 (1932); J. G. Kirkwood, *ibid.* 44, 31 (1933).

[4] H. E. DeWitt, J. Math. Phys. 3, 1003 (1962).

[5] S. Y. Larsen, J. E. Kilpatrick, E. H. Lieb, and H. F. Jordan, Phys. Rev. 140, A129 (1965).

[6] The first Green's function approach to the problem of hard spheres was obtained by T. D. Lee (unpublished). A derivation of Eq. (2) is given in M. E. Boyd, S. Y. Larsen, and J. E. Kilpatrick, J. Chem. Phys. 45, 449 (1966). For the connection with diffusion theory see A. Pais and G. E. Uhlenbeck, Phys. Rev. 116, 250 (1959).

[7] Another available technique is to express $B(T)$ in terms of phase shifts and bound states of the potential. But to extract the first-order quantum correction in this way is rather tedious even in one dimension [Dr. Alba Theumann (private communication)].

[8] The Laplace transform is found in Bateman Project Tables, edited by H. Erdely (McGraw-Hill Book Company, Inc., New York, 1954), Vol. I, p. 146. For the transition from Eq. (9) to Eq. (10) we have used the special case $\mu=0$, $\nu=\frac{1}{2}$ of § 13.43 (2) of G. N. Watson, A Treatise on the Theory of Bessel functions (Cambridge University Press, Cambridge, 1944).

[9] F. Mohling, Phys. Fluids 6, 1097 (1963), calculated the term in Eq. (16) corresponding to the quantum correction due to the hard core. He argued that this was the dominating contribution at high temperatures. Our result shows that at high temperatures the remaining contribution is $\sim\frac{1}{8}\eta^2(u/kT)^2$ of the hard-core contributions.

[10] G. E. Uhlenbeck and E. Beth, Ref. 2.