a region where the JWKB asymptotic solutions are no longer valid.[4] However, we believe that this difficulity can be treated using a modified form of the Miller–Good method.[5]

III. DISCUSSION

The results of this calculation show that the first quantum correction for a hard-core-plus-attractive-well potential is independent of the shape of the well, and depends only on the value of the potential at the core. Thus for any potential, square well, triangular well, etc., which is continuous near the core, the first quantum correction is given by the term[6]

$$\frac{3}{2\sqrt{2}}\,[\beta v(a)]\left(\frac{\lambda}{a}\right) \quad .$$

Hence, classical arguments alone should suffice in distinguishing which potential-well model best fits experimental data at high temperatures, at least to $O(\lambda^4/a^4)$.

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[4] The author is indebted to Dr. M. Barnhill for discussion on this point.

[5] S. C. Miller and R. H. Good, Phys. Rev. 91, 174 (1953).

[6] W. G. Gibson [following paper, Phys. Rev. A 7, 822 (1973)] has also obtained this result using a somewhat different method.

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Quantum Corrections to the Virial Coefficients for Potentials with Hard Cores

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The leading quantum correction to the virial coefficients is calculated for the case where the intermolecular potential has a hard core. If the potential is bounded and continuous outside the core, the leading quantum correction to the second virial coefficient comes entirely from the region of the hard-core boundary, and depends only on the diameter of the core and the depth of the potential well at the core boundary. The leading quantum correction to the higher virial coefficients also involves the value of the classical radial distribution function at the core boundary. If the potential has discontinuities outside the core, these will give rise to additional first-order corrections.

We investigate the leading quantum correction to the virial coefficients for the case where the intermolecular potential has a hard core. The standard Wigner–Kirkwood method cannot be used, since it requires that the potential be differentiable. Instead we use the method developed in a previous paper[1] (hereafter referred to as I) which is valid for a general potential. The basic quantity is the thermal Green's function $G(\vec{r},\vec{r};\ \beta)$, and this is calculated in the approximation where the curvature of the potential boundaries is neglected. This enables us to obtain the quantum corrections to the virial coefficients to first order in the thermal wavelength λ.

The intermolecular potential is taken to be of the form

$$v(r) = \infty, \qquad r < a$$
$$v(r) = v_1(r), \quad r > a \tag{1}$$

where $v_1(r)$ is bounded, and decreases rapidly enough as $r \to \infty$ for the virial coefficients to exist. We wish to calculate $\lambda^3 G(\vec{r}, \vec{r}; \beta)$ correct to first order in λ. [$\lambda = (2\pi\hbar^2\beta/m)^{1/2}$ where $\beta = 1/kT$.] From Appendix B of I,

$$G(\vec{r}, \vec{r}; \beta) \sim -\frac{1}{2\lambda^2}\frac{1}{2\pi i}\int_{c-i\infty}^{c+i\infty} dp\, e^{\alpha p}\overline{G}_1(r, r; \gamma) , \tag{2}$$

where $\gamma = p^{1/2}$ and $\alpha = \lambda^2/2\pi$. $\overline{G}_1(r, r; \gamma)$ is the Green's function for the one-dimensional Schrödinger equation and can be constructed according to the formula

$$\overline{G}_1(r', r; \gamma) = [W(u_1, u_2)]^{-1} u_1(r_<) u_2(r_>) . \tag{3}$$

u_1, u_2 are solutions of

$$\left(-\frac{d^2}{dx^2} + \frac{m}{\hbar^2} v(x) + \gamma^2\right) u(x) = 0 , \tag{4}$$

satisfying the boundary conditions $u_1(a) = 0$, $u_2(r) \to 0$ as $r \to \infty$; $W(u_1, u_2) = u_1 u_2' - u_1' u_2$ is their Wronskian.

A solution of (4) valid for large γ can be obtained using the WKB method.[2] Since we are working at large negative energies there are no turning points, and the solution for $r > a$ is

$$u(r) = q^{-1/2}\left[A \exp\left(\int^r q\, dr\right) + B \exp\left(-\int^r q\, dr\right)\right] \times\left[1 + O\left(\frac{1}{\gamma}\right)\right] , \tag{5}$$

where

$$q \equiv q(r) = [\gamma^2 + m v_1(r)/\hbar^2]^{1/2} \tag{6}$$

and A and B are arbitrary constants. To the same order, the derivative is

$$u'(r) = q^{1/2}\left[A \exp\left(\int^r q\, dr\right) - B \exp\left(-\int^r q\, dr\right)\right] \times\left[1 + O\left(\frac{1}{\gamma}\right)\right] . \tag{7}$$

If we now require that the potential $v(r)$ be continuous (as well as bounded) for $r > a$, then $u(r)$ and $u'(r)$, as given by (5) and (7), are also continuous for $r > a$, and can be used to construct the Green's function. A straightforward calculation gives

$$\overline{G}_1(r, r; \gamma) = 0, \qquad r < a$$
$$\overline{G}_1(r, r; \gamma) = -\left(\frac{1}{2q}\right)\left[1 - \exp\left(-2\int_a^r q\, dr\right)\right] \times\left[1 + O\left(\frac{1}{\gamma}\right)\right], \quad r > a . \tag{8}$$

For γ large,

$$\exp\left(-2\int_a^r q\, dr\right) \sim \exp[-2q(a+)(r - a)] \sim \tfrac{1}{2}[q(a+)]^{-1}\delta(r - a+) , \tag{9}$$

where $\delta(r - a+)$ is a Dirac δ function. Thus

$$\overline{G}_1(r, r; \gamma) = -\tfrac{1}{2}[q(r)]^{-1} + \tfrac{1}{4}[q(a+)]^{-2} \times\delta(r - a+) + O(\gamma^{-3}) , \quad r > a . \tag{10}$$

Inserting (10) into (2) and doing the inverse Laplace transform integral gives

$$G(\vec{r}, \vec{r}; \beta) = 2^{-3/2}\lambda^{-3}e^{-\beta v(r)} \times[1 - 2^{-3/2}\lambda\delta(r - a+) + O(\lambda^2)] . \tag{11}$$

Note that the right-hand side of (11) is simply $e^{-\beta v(r)}$ times the thermal Green's function for hard spheres of diameter a. This is a reasonable result, as can be seen from the relation

$$G(\vec{r}', \vec{r}; \beta) = \langle \vec{r}' | e^{-\beta H_{\rm rel}} | \vec{r} \rangle , \tag{12}$$

where $H_{\rm rel}$ is the Hamiltonian for the relative motion of the two-particle system.

The direct part of the second virial coefficient is given by

$$B_{\rm dir} = \tfrac{1}{2}\int d^3r[1 - 2^{3/2}\lambda^3 G(\vec{r}, \vec{r}; \beta)] . \tag{13}$$

Using (11), we find

$$B_{\rm dir} = B_{\rm class} + \frac{2\pi a^3}{3}\,\frac{3}{2\sqrt{2}}\, e^{-\beta v(a+)}\left(\frac{\lambda}{a}\right) + O(\lambda^2) , \tag{14}$$

where

$$B_{\rm class} = \tfrac{1}{2}\int d^3r(1 - e^{-\beta v(r)}) \tag{15}$$

is the usual classical second virial coefficient. Thus the first-order quantum correction to $B_{\rm dir}$ comes entirely from the region near the hard core. It depends on $v(a+)$, the value of the potential just outside the core, but is independent of the detailed nature of the rest of the potential, provided only that it is bounded and continuous for $r > a$. In particular, the result (14) applies to the hard-core–plus–attractive-well potential, and is in agreement with a recent calculation by D'Arruda[3] for this potential model.

Expressions for the quantum corrections to the higher virial coefficients can also be found, following the method of I. The quantity c_2, defined by Eq. (19) of I, is found to be

$$c_2 = -2^{-1/2}\pi a^2 g(a+)\lambda + O(\lambda^2) , \tag{16}$$

where $g(r)$ is the classical radial distribution function. The pressure is now given by (21) of I:

$$\beta p = \beta p^c - \rho^2\frac{\partial(\rho c_2)}{\partial\rho} + O(\lambda^2) , \tag{17}$$

where p^c is the pressure of the classical gas and ρ is the number density. If we expand the pressure in a virial series,

$$\beta p = \rho + \sum_{n=2}^{\infty} B_n \rho^n , \tag{18}$$

with a corresponding equation for p^c, and the radial distribution function in a density series,

$$g(r) = e^{-\beta v(r)} \sum_{n=0}^{\infty} \rho^n y_n(r) , \tag{19}$$

then substituting in (17) and equating powers of ρ gives

$$B_n = B_n^c + (n-1)2^{-1/2}\pi a^2 e^{-\beta v(a+)} y_{n-2}(a)\lambda + 0(\lambda^2) . \tag{20}$$

B_n is the direct part of nth virial coefficient and B_n^c is its classical counterpart. $y_0(r) = 1$, so for $n = 2$ (20) reduces to (14). For $n > 2$, $y_{n-2}(a)$ depends on the detailed nature of the potential, so for virial coefficients higher than the second the leading quantum correction is not determined solely by the depth of the potential at the hard core.

If the potential fails to be continuous for $r > a$, there will be additional first-order quantum corrections from the neighborhood of the discontinuities. For example, for the square-well potential

$$\begin{aligned} v(r) &= \infty , & r &< a \\ v(r) &= -\epsilon , & a &< r < b \\ v(r) &= 0 , & r &> b , \end{aligned} \tag{21}$$

the nth virial coefficient is[1]

$$B_n = B_n^c + (n-1)2^{-1/2}\pi[a^2 e^{\beta\epsilon} y_{n-2}(a) + b^2\theta(\beta\epsilon) y_{n-2}(b)]\lambda + O(\lambda^2) , \tag{22}$$

where

$$\theta(x) \equiv 1 + e^x - 2e^{x/2} I_0(\tfrac{1}{2}x) . \tag{23}$$

Comparing (22) with (20) shows that the contribution from the neighborhood of the hard core is the same in each case, but we now have an additional contribution from the discontinuity at $r = b$.

In the above we have considered only the first-order quantum correction to the virial coefficients. Higher-order corrections to the second virial coefficient can be obtained using its expression as the inverse Laplace transform of the logarithmic derivative of the Jost function,[4] and this is the method employed by D'Arruda in his calculation for the hard-core-plus-attractive-well potential.[3] Another possible method is the modified Wigner–Kirkwood expansion given recently by Derderian and Steele,[5] in which hard-sphere basis functions rather than free-particle functions are used.

For the higher coefficients, the only method available seems to be that of I. The theory given there is quite general, and includes all higher corrections. However, even for the second-order term computational difficulties are severe. Not only does one require $G(\vec{r}, \vec{r}; \beta)$ to the next order, but one also needs the leading term in the function $U_3^m(1, 2, 3)$, and this involves solving a three-body problem.[6]

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Variation-Iteration Solution of the Variable-Phase Equation

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It is pointed out that the variation-iteration method offers a fast and accurate means for solving the variable-phase equation. The method is especially useful for problems involving many partial waves.

In a recent paper by Landman,[1] a perturbation-variation treatment of the variable-phase function has been proposed. The method consists of two parts. First, the standard technique of perturbation theory is applied to the variable-phase equation.[2] A variational principle[3] is then employed to optimize the choice for the main part of the potential.

We wish to point out the limitations of Landman's method and offer a remedy. We shall adopt Land-