

Quantum corrections to the second virial coefficient in one dimension

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The semiclassical limit of the quantum mechanical second virial coefficient in one dimension is examined using realistic interatomic potentials for ^4He , H_2 , and ^{20}Ne . A direct transcription from three dimensions of the quantum correction series through \hbar^4 gives results for B_2 within 0.5% of those from the phase shift calculations for ^4He at 50 K and ^{20}Ne at 30 K.

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I. INTRODUCTION

Although many statistical mechanical formulations are simply adapted from three to two to one spatial dimension, there are exceptions. One that recently drew attention^{1,2} is the expression for the quantum mechanical second virial coefficient $B_2(T)$ for hard-core particles in one dimension (1D). In this case, Gibson's result,³

$$B_2(T) = \frac{\Lambda}{4} - \Lambda \sum_b \exp(-\beta\epsilon_b) - \frac{\Lambda}{\pi} \int_0^\infty \frac{d\eta}{dk} \exp\left(-\frac{\beta\hbar^2 k^2}{2\mu}\right) dk, \quad (1)$$

has a novel term $\Lambda/4$ which has the appearance of a quantum statistics exchange term, although the exchange second virial coefficient vanishes for the 1D gas with impenetrable (i.e., negligible tunneling) pair potentials. In Eq. (1), $\Lambda = \hbar\sqrt{2\pi\beta/\mu}$ is the thermal wavelength for relative motion of particles of mass m , reduced mass $\mu = m/2$, and ϵ_b and $\eta(k)$ are the bound state energies and scattering phase shift. Equation (1) has been evaluated¹ for ^4He atoms moving in 1D at temperatures below 10 K, corresponding to conditions for adsorption on carbon nanotube bundles.

The question arises what the semiclassical limit is for $B_2(T)$ given by Eq. (1). For motion in three dimensions (3D), semiclassical approximations drastically simplify the calculations for sufficiently high temperatures,^{4,5} about 50 K for ^4He and H_2 and 20 K for ^{20}Ne . It was not known what changes in the limit behavior arise from the $\Lambda/4$ term for the 1D case. Our result, Sec. II, is that the fully quantum mechanical calculations with Eq. (1) are closely approximated by a direct transcription of the semiclassical 3D Wigner-Kirkwood (WK) results⁶ for the \hbar^0 , \hbar^2 , and \hbar^4 contributions, i.e., the $\Lambda/4$ is canceled by contributions from the rest of Eq. (1). However, the $\Lambda/4$ remains, Sec. III, in the leading (\hbar) quantum correction for B_2 for a hard-rod-plus-square-well potential.⁷

II. CALCULATIONS FOR HELIUM, HYDROGEN, AND NEON

Calculations using Eq. (1) entail numerical solutions for the dimer bound state energies and for the scattering phase shifts carried to large enough wave number that the integral converges. We performed these calculations for three realis-

tic interatomic potential models that are known to reproduce a large range of 3D scattering and thermodynamic data. For all three cases, ^4He , H_2 , and ^{20}Ne , convergence at 100 K is assured by carrying the integrations to $k=40 \text{ \AA}^{-1}$. There is one bound state for ^4He using the TTY potential,⁸ one bound state for spherical H_2 using the Silvera-Goldman potential,⁹ and three bound states for ^{20}Ne using the HFD-B potential.¹⁰

The WK semiclassical series⁶ for 1D motion with a smooth interatomic potential $\phi(x)$ is

$$B_{sc}(T) \equiv B_{cl}(T) + (\hbar^2/m)B_{q1}(T) + (\hbar^2/m)^2 B_{q2}(T), \quad (2)$$

$$B_{cl} = \int_0^\infty \{1 - \exp[-\beta\phi(x)]\} dx, \quad (3)$$

$$B_{q1} = \frac{\beta^3}{12} \int_0^\infty \exp[-\beta\phi(x)] [d\phi/dx]^2 dx, \quad (4)$$

$$B_{q2} = -\frac{\beta^4}{120} \int_0^\infty \exp[-\beta\phi(x)] \left((d^2\phi/dx^2)^2 - \frac{5}{36} \beta^2 (d\phi/dx)^4 \right) dx. \quad (5)$$

The series converges quite rapidly for the higher temperatures in Table I as judged by the sizes of the successive terms and by comparing to results of the phase shift calculation. ^4He and ^{20}Ne are the most quantum and most classical of the species, respectively. B_2 and B_{sc} agree to 8% at 20 K and 0.5% at 50 K for ^4He , and 2% at 20 K and 0.5% at 50 K for ^{20}Ne . Thus, the numerical study clearly establishes that the $\Lambda/4$ term is not to be added to the usual \hbar^2 series. It has been offset by contributions from the other terms in Eq. (1) because it alone would be a 20% correction for ^4He in this range and 15% for ^{20}Ne . On the other hand, if the $\Lambda/4$ term were omitted from Eq. (1), the results would violate the bound² $B_2 > B_{cl}$ for many of the cases in Table I.

III. HARD ROD PLUS SQUARE WELL

The interaction is

$$\begin{aligned} \phi(x) &= \infty, & |x| < a \\ &= -\epsilon, & a < |x| < b \\ &= 0, & b < |x|. \end{aligned} \quad (6)$$

TABLE I. Second virial coefficient in 1D as a function of temperature T , in $\text{\AA}/\text{atom}$ for helium and neon and $\text{\AA}/\text{molecule}$ for hydrogen. B_2 is the quantum mechanical result, Eq. (1), B_{cl} is the classical approximation, Eq. (3); and B_{sc} is the WK semiclassical approximation through \hbar^4 , Eq. (2). The pair potentials are the Tang-Toennies-Yiu (TTY) model⁸ for He, the spherical Silvera-Goldman model⁹ for H_2 , and the HFD-B model of Aziz and Slaman¹⁰ for Ne.

T (K)	^4He			H_2			^{20}Ne		
	B_2	B_{sc}	B_{cl}	B_2	B_{sc}	B_{cl}	B_2	B_{sc}	B_{cl}
10	2.13	-0.58 ^a	0.84	-2.34	-179 ^a	-18.8	-18.60	-24.91	-31.25
20	2.28	2.12	1.82	0.67	-2.02 ^a	-1.60	-1.79	-1.83	-2.56
30	2.32	2.28	2.05	1.47	1.12	0.52	0.36	0.36	0.13
40	2.33	2.32	2.15	1.83	1.73	1.28	1.13	1.13	1.01
50	2.33	2.32	2.19	2.03	1.99	1.65	1.51	1.51	1.44
100	2.30	2.30	2.24	2.37	2.37	2.24	2.11	2.11	2.09

^aIn these cases $B_{sc} < B_{cl}$ and B_{sc} is inferior to B_{cl} as an estimate for B_2 .

The solution for the second virial coefficient in the semiclassical limit is

$$B_2(T) \approx [a - (b - a)(e^{\beta\epsilon} - 1)] + \frac{\Lambda}{4} + \frac{\Lambda}{2} e^{\beta\epsilon} [1 - e^{-\beta\epsilon/2} I_0(\beta\epsilon/2)], \quad \hbar \rightarrow 0, \quad (7)$$

where the first line is the classical value of B_2 and the second line is the first quantum correction, linear in \hbar ; I_0 is the order zero modified Bessel function of the first kind. For $\epsilon=0$, Eq. (7) is the exact second virial coefficient for hard rods.^{2,7}

We derived Eq. (7) in two ways. One was to evaluate the Green's function $\langle x | \exp(-\beta H) | x \rangle$ by adapting Gibson's asymptotic 3D calculation;⁷ then the linear \hbar terms in B_2 arise from the discontinuities in the potential at $x=a$ and $x=b$. The second, more intricate, method was to make asymptotic estimates directly for the bound state sum and phase shift integral in Eq. (1), as outlined in the Appendix. The two methods agreed in the semiclassical limit, after the coefficient of an oscillatory term in the phase shift analysis vanished. However, as for 3D, the semiclassical limit of B_2 for this discontinuous potential has a qualitatively different structure than for the smooth potentials characteristic of inert gas interactions.

A question may arise whether the usual implementation of the phase shift calculations by using a hard core (vanishing wave function) boundary condition at a very small separation $x=a$ introduces a spurious linear \hbar term in the numerical results. It does not. The coefficient of such a term is shown to be exceedingly small, proportional to $\exp[-\beta v(a^+)]$, by the 1D version of an algebraic 3D analysis.¹¹ Alternatively, the hard core distance is decreased until there is no visible effect in the numerical results, as was done for Sec. II.

IV. CONCLUSIONS

This work shows the validity of the WK approximation for the semi-classical limit of $B_2(T)$ of the 1D quantum gas, although the analytical structure of the quantum theory³ might have raised doubts. Approximations based on the

Green's function, such as the WK series and the first quantum correction for hard-rod-plus-square-well,⁷ transfer readily from 3D to 1D. Further, the full quantum calculations with Eq. (1) are quite straightforward for the cases in Table I. However, the WK series is easier to apply when the physical situation is only quasi-one-dimensional. The grooves formed by parallel adjacent nanotubes at the external surface of carbon nanotube bundles are believed¹² to support 1D adsorbed phases at temperatures below 10 K. At temperatures above 20 K the transverse degrees of freedom are no longer frozen out for some adsorbates.¹³ Then a WK approximation to the Green's function may enable estimates of the size of the deviations from the ideal 1D behavior.

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APPENDIX: DERIVATION OF EQ. (7)

The asymptotic analysis for Eq. (7) consists of separate reductions of bound state and scattering terms B_b and B_s , defined in Eqs. (A4) and (A7). Let $\ell = b - a$ and $\gamma = \sqrt{2\mu\epsilon\ell^2/\hbar^2}$.

The bound state energies $\epsilon_b \equiv -\epsilon[1 - (\xi/\gamma)^2]$ use the roots ξ_n of

$$\xi \cot \xi = -\sqrt{\gamma^2 - \xi^2}. \quad (\text{A1})$$

For large γ the ξ_n are well approximated by

$$\xi_n \approx n\pi - \delta_n, \quad (\text{A2})$$

$$\delta_n = \tan^{-1}[(n\pi)/\sqrt{\gamma^2 - (n\pi)^2}]. \quad (\text{A3})$$

The enumeration of bound states is $n=1, \dots, n_M$, where $n_M = n_j$ for $n_j\pi < \gamma < (n_j + \frac{1}{2})\pi$ and $n_M = n_j + 1$ for $(n_j + \frac{1}{2})\pi < \gamma < (n_j + 1)\pi$. The bound state sum is

$$\begin{aligned}
B_b &\equiv -\Lambda \sum_b \exp(-\beta\epsilon_b) \\
&\simeq -\Lambda e^{\beta\epsilon} \sum_{j=1}^{n_M} \exp[-\beta\epsilon(j\pi/\gamma)^2][1 + (2\beta\epsilon/\gamma^2)j\pi\delta_j].
\end{aligned}
\tag{A4}$$

After approximating the sum by an integral and including the leading Euler-Maclaurin corrections the estimate for B_b is

$$\begin{aligned}
B_b &\simeq -\frac{\Lambda\gamma}{\pi} e^{\beta\epsilon} \int_0^1 \exp(-\beta\epsilon\xi^2) d\xi + \frac{\Lambda}{2} [e^{\beta\epsilon} - e^{\beta\epsilon/2} I_0(\beta\epsilon/2)] \\
&\quad + \frac{\Lambda}{\pi} [\gamma - n_M\pi],
\end{aligned}
\tag{A5}$$

where the first line contributes to the classical \hbar^0 term and the last term in the second line arises from the offset of the bound state count n_M relative to the binding parameter γ .

Define a scaled wave number $\xi = k\ell$ and rewrite the scattering phase shift as $\eta(k) = -(\xi b/\ell) + \chi(\xi)$ where $\chi(\xi)$ is the solution of

$$\xi \cot \chi = \sqrt{\gamma^2 + \xi^2} \cot \sqrt{\gamma^2 + \xi^2}.
\tag{A6}$$

The scattering integral is then

$$\begin{aligned}
B_s &\equiv -\frac{\Lambda}{\pi} \int_0^\infty \frac{d\eta}{dk} \exp\left(-\frac{\beta\hbar^2 k^2}{2\mu}\right) dk \\
&= b - \frac{\Lambda}{\pi} \int_0^\infty \frac{d\chi}{d\xi} \exp\left(-\frac{\beta\hbar^2 \xi^2}{2\mu\ell^2}\right) d\xi.
\end{aligned}
\tag{A7}$$

For large γ , the $d\chi/d\xi$ term contributes both in $O(\hbar^0)$ and in cancelling the last term in Eq. (A5):

$$B_s = b - \frac{\Lambda\gamma}{\pi} e^{\beta\epsilon} \int_1^\infty \exp(-\beta\epsilon\xi^2) d\xi - \Lambda F(\gamma, \beta\epsilon),
\tag{A8}$$

where

$$\begin{aligned}
F(\gamma, V) &= \frac{\gamma}{\pi} \int_0^\infty \exp(-V\xi^2) \left[-\frac{\xi}{\sqrt{1+\xi^2}} \right. \\
&\quad \left. + \frac{1}{\xi^2 + \cos^2 \gamma\sqrt{1+\xi^2}} \left(\xi^2 + \frac{\sin 2\gamma\sqrt{1+\xi^2}}{2\gamma\sqrt{1+\xi^2}} \right) \right] d\xi.
\end{aligned}
\tag{A9}$$

For $V \rightarrow 0$, the contribution of F cancels the last term in Eq. (A5) and the net result is Eq. (7). For $V < 1$, the cancellation remains nearly complete.

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