Comment on "Quantum virial expansion approach to thermodynamics of ^{4}He adsorbates in carbon nanotube materials: Interacting Bose gas in one dimension"

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It is shown that the exchange term in the quantum mechanical second virial coefficient B_2 vanishes for hard-core particles moving in only one dimension. The formulation of B_2 as an integral over scattering phase shifts is discussed.

I. INTRODUCTION

There is a dictum that there are no observable effects of quantum statistics for hard-core particles in one dimension. Inert gas systems that are effectively one-dimensional now can be realized[1] and the quantum mechanical second virial coefficient $B_2(T)$ has been evaluated[2] for ^{4}He in one dimension. Thus, it is timely to examine how that dictum is satisfied for $B_2(T)$ of a one-dimensional quantum gas and, more generally, to review the formulation[3] of B_2 in terms of scattering phase shifts. Note, however, that exchange terms do remain in more general correlation functions such as the momentum distribution.[4]

The quantum mechanical second virial coefficient at temperature T in d-dimensions is[5]

$$B_2(T) = B_d(T) \pm \frac{1}{2S+1} B_e(T), \qquad (1)$$

for particles of spin S and mass m, where the upper/lower sign applies for fermions/bosons, respectively. The direct and exchange terms are given by

$$B_d(T) = -\frac{1}{2}\Lambda^d \int d^d x \langle \mathbf{x}|e^{-\beta H} - e^{-\beta H_0}|\mathbf{x}\rangle \qquad (2)$$

and

$$B_e(T) = \frac{1}{2}\Lambda^d \int d^d x \langle -\mathbf{x}|e^{-\beta H}|\mathbf{x}\rangle, \qquad (3)$$

where the thermal wavelength for reduced mass $\mu = m/2$ is $\Lambda = \hbar\sqrt{2\pi\beta/\mu}$ and the free and interacting-particle Hamiltonians for relative motion are $H_0 = p^2/2\mu$ and $H = H_0 + V(|\mathbf{x}|)$.

For ^{4}He, it has been shown by calculation in two[6] and three[5] dimensions, $d=2$ and $d=3$, that $B_e(T)$ effectively is absent, exponentially small, except at low temperatures where Λ becomes larger than the core radius a in the pair potential. This is explained[7] in terms of the requirement that the exchange paths from $\mathbf{x}$ to $-\mathbf{x}$ in a path integral form[8] of B_e must avoid the hard core and have a minimum length πa, so that $B_e \propto \exp(-\pi^3 a^2/\Lambda^2)$. For $d=1$ there are no paths that avoid the hard core and the conclusion is even stronger, $B_e = 0$, in accord with the more general rule stated at the outset.

In Sec. II, this result is obtained by a second argument and the relation to results[2] for a more realistic model[9] of ^{4}He is discussed. In Sec. III, the use of scattering phase shifts to evaluate B_d is reviewed.

II. $B_2(T)$ FOR ^{4}HE IN ONE DIMENSION

A second derivation of the absence of an exchange term for hard-core potentials in $d=1$ uses properties of the eigenfunctions $\psi_j(x)$ in a Slater-sum representation for the terms in the integrands of Eqs. (2) and (3):

$$\langle x|\exp(-\beta H)|y\rangle = \sum_j \psi_j^*(x)\psi_j(y)\exp(-\beta E_j). \qquad (4)$$

For a potential with a hard core of radius a, the eigenstates are doubly degenerate and the even and odd parity normalized wave functions[3] can be expressed in terms of u_j for $0 < x < \infty$ by

$$\psi_{j\pm}(x) = (1/\sqrt{2})[u_j(x) \pm u_j(-x)], \qquad (5)$$

because there is no overlap, $u_j(x)u_j(-x)=0$ for $x \neq 0$. The combination $\psi_{j+}(-x)\psi_{j+}(x) + \psi_{j-}(-x)\psi_{j-}(x)$ vanishes and $B_e = 0$.

The arguments thus far assume that the pair potential has a hard core, $V(x) \rightarrow \infty$ for $|x| < a$. The situation for realistic helium pair potentials[9] is not so extreme. However, solutions for the scattering wave functions at energies in the range 1–100 K show that there is a negligible effect of tunneling through the core. For instance, changing the starting point in the numerical integration from $x=1.3$ Å to $x=1.0$ Å ($V > 10^4$ K) changes the calculated phase shift by less than 1 part in 10^6. Thus B_e must be negligibly small.

The conclusion is that the ideal gas exchange term should be omitted from the calculation of $B_2(T)$ for ^{4}He in $d=1$, i.e., $B_2 = B_d$. Further, because the classical second virial coefficient is a lower bound[10] to B_d,

$$B_d(T) \geqslant -\frac{1}{2}\int_{-\infty}^{\infty}[\exp\{-\beta V(x)\}-1]dx = B_{2,cl}(T) \ (d=1) \qquad (6)$$

there is a bound $B_2(T) \geqslant B_{2,cl}(T)$. This was applied to a calculation of the total second virial coefficient for the SAPT1 potential[9] used by Šiber.[2] At $T=10$ K, the classical calcula-

tion gives $B_2 \geqslant 0.84$ Å/atom while Šiber's result is $B_2 = 0.1$ -0.2 Å per atom. Therefore something has slipped in his calculation. The error is identified in Sec. III.

III. FORMULATION OF B_2 USING PHASE SHIFTS

The expression that Šiber gives for B_2 has an appearance quite similar to that used in $d=2$ and $d=3$. In the present notation it is

$$B_2(S) = -\frac{\Lambda}{4} - \Lambda \sum_b \exp(-\beta \epsilon_b)$$
$$- \frac{\Lambda}{\pi} \int_0^\infty \frac{d\eta}{dk} \exp\left(-\frac{\beta \hbar^2 k^2}{2\mu}\right) dk. \quad (7)$$

The first term on the right-hand side is equal to the second virial coefficient for an ideal gas of $S=0$ bosons. The second term is a sum over bound states, with energies ϵ_b, of the pair potential and the third term arises from the change in the density of two-body states, expressed using the scattering phase shift $\eta(k)$.

There is a problem with Eq. (7) that can be seen by using it to calculate B_2 for the hard-rod gas,[4,11] with potential $\phi(r) = \infty, |x| < a; =0, |x| > a$. The phase shift for this case has $d\eta/dk = -a$ and the result from Eq. (7) is $B_2(S) = a - (\Lambda/4)$. On the other hand, using Eqs. (1)–(3) and the analytical expressions for the Green's functions[4] gives $B_2 = a + (\Lambda/4)$.

The source of the difference can be located by expressing B_d in terms of the partition functions for relative motion of the ideal and hard-rod gases, both confined in a long box $(-L, L)$. Then the sum-over-states gives

$$B_2 = B_d = -\frac{\Lambda}{2}\left[2 \sum_{n_1=1}^\infty \exp\left(-\frac{\beta \hbar^2 \pi^2}{2\mu(L-a)^2} n_1^2\right) \right.$$
$$\left. - \sum_{n_2=1}^\infty \exp\left(-\frac{\beta \hbar^2 \pi^2}{8\mu L^2} n_2^2\right) \right] \quad (8)$$

$$= a + \frac{\Lambda}{4} \quad L \to \infty, \quad (9)$$

where the explicit eigenstate energies for a particle in a box are used and the factor 2 in the first term on the right-hand side of Eq. (8) arises from the degeneracy of states discussed in Eq. (5). The Euler-Maclaurin summation formula has been used to convert the sums to integrals and the last term in Eq. (9) is the only surviving correction term to the integrals.[12]

The corresponding modification for more general cases with hard-core potentials was given already by Gibson[3]

$$B_2 = B_d = \frac{\Lambda}{4} - \Lambda \sum_b \exp(-\beta \epsilon_b) - \frac{\Lambda}{\pi} \int_0^\infty \frac{d\eta}{dk} \exp\left(-\frac{\beta \hbar^2 k^2}{2\mu}\right) dk. \quad (10)$$

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