Semiclassical corrections to the interaction energy of a hard-sphere Boltzmann gas

R K Bhaduri†, W van Dijk‡, and M K Srivastava§

† Department of Physics and Astronomy, McMaster University, Hamilton, Canada L8S 4M1
‡ Physics Department, Redeemer University College, Ancaster, Canada L9K 1J4
§ Institute Instrumentation Center, IIT, Roorkee 247667, India

E-mail: bhaduri@physics.mcmaster.ca, vandijk@physics.mcmaster.ca

Abstract. Quantum effects in statistical mechanics are important when the thermal wavelength is of the order of, or greater than, the mean interatomic spacing. This is examined at depth taking the example of a hard-sphere Boltzmann gas. Using the virial expansion for the equation of state, it is shown that the interaction energy of a classical hard-sphere gas is exactly zero. When the (second) virial coefficient of such a gas is obtained quantum mechanically, however, the quantum contribution to the interaction energy is shown to be substantial. The importance of the semiclassical corrections to the interaction energy shows up dramatically in such a system.

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1. Introduction

The virial expansion of a dilute gas is standard fare in the curriculum of the statistical mechanics course for beginning graduate students. The hard-sphere classical gas provides a nice example on this topic, since the first few classical virial coefficients are analytically known. The quantum corrections in the dilute hard-sphere gas, however, is a topic not covered in text books.

The objective of this paper is to study the quantum corrections in a hard-sphere one-component Boltzmann gas. The usefulness of semiclassical approximations in understanding the difference between the classical and quantum results is demonstrated in this paper. As usual, we consider the gas in the thermodynamic limit, where the number of atoms (of one kind only), $N \to \infty$, as also the volume of the enclosure, $V \to \infty$, but the number density $n = N/V$ remains finite. Each atom is taken to be a rigid (impenetrable) sphere of diameter $a$, so that the minimum relative distance between the spheres is $a$. It must be mentioned at the outset that this system has been studied extensively in the last fifty years (see [1] for a nice summary). Semiclassical quantum corrections in the hard-sphere Boltzmann gas were examined (amongst others) by Hill [2] and Gibson [3]. Our focus in this paper will be mainly on the interaction energy of the hard-sphere gas. We first show, using the virial expansion for the equation of state, that this is exactly zero when the virial coefficients for the hard-sphere gas are calculated classically. Since we consider a Boltzmann gas, there are no exchange contributions due to statistics. For a dilute gas at high temperature, it is the second virial coefficient that gives the dominant contribution. The second virial coefficient may also be calculated quantum mechanically from the Beth-Uhlenbeck formula using the hard-sphere scattering phase shifts in the various partial waves [4]. Contrary to naive expectations, the quantum result for the interaction energy of the Boltzmann gas at high temperatures is substantially different from the classical one, even when the thermal wavelength is only a fraction of the hard-sphere diameter. Obtaining the quantum result requires careful numerical work, adding contributions from more and more partial waves with increasing temperature. The difference between the quantum and the classical results may be accounted for by the semiclassical corrections, given in the form of an asymptotic series. This example shows the usefulness of the semiclassical method in statistical mechanics even for a singular interaction.

2. The interaction energy

2.1. The virial expansion

To appreciate this in more detail, note that the virial expansion of a (one-component) gas (classical as well as quantal) for the pressure $P$ at a temperature $T$ is given by [5]

$$\frac{P}{nT} = 1 + a_2(n\lambda^3) + a_3(n\lambda^3)^2 + \cdots,$$

(1)
where $a_2, a_3, \ldots$, are the dimensionless second, third, etc., virial coefficients, $\tau = k_B T$, $n = N/V$ is the number density of particles, and $\lambda = \sqrt{2\pi\hbar^2/m\tau}$ is the thermal wavelength. Even for an ideal quantum gas of bosons or fermions, the virial coefficients are nonzero. These contributions due to statistics will not be included in our Boltzmann gas; only the part due to the interaction between the atoms will be considered. The free energy $F = E - TS$ may be easily obtained by integrating the above $P$ with respect to the volume $V$ (since $P = -\left(\partial F/\partial V\right)_\tau$), the constant of integration being chosen to match the perfect Boltzmann gas value:

$$F = -N\tau \ln \left(\frac{V}{\lambda^3}\right) + a_2\lambda^3\tau \frac{N^2}{V} + \cdots + a_j\lambda^{3(j-1)}\tau \frac{N^j}{(j-1)V^{j-1}} + \cdots. \quad (2)$$

The energy may next be obtained by using the relation $E = -\tau^2\left(\partial(F/\tau)/\partial\tau\right)$. After subtracting out the energy of the perfect gas part, one obtains the virial series for the interaction energy per particle:

$$\frac{E_{\text{int}}}{N} = 3\frac{\tau}{2} \left\{ (n\lambda^3) \left[ a_2 - \frac{2}{3}\tau \frac{da_2}{d\tau} \right] + (n\lambda^3)^2 \left[ a_3 - \frac{2}{3}\tau \frac{da_3}{d\tau} \frac{1}{2} \right] + \cdots \right. \\
+ (n\lambda^3)^{(j-1)} \left[ a_j - \frac{2}{3}\tau \frac{da_j}{d\tau} \frac{1}{j-1} \right] + \cdots \right\}. \quad (3)$$

The above equation for the interaction energy, modified for a two-component Fermi gas, has been used recently by Ho and Mueller [6]. Whereas for a classical gas the virial coefficients may be expressed as integrals involving the interaction potential, for the quantum problem a solution of the $j$-body problem is needed to obtain $a_j$. Henceforth we shall denote the classical virial coefficients by $A_j$ to differentiate from their quantum counterparts, to be still denoted as $a_j$.

It is easy to see now why the interaction energy for a classical hard-sphere gas is zero order by order, in every power of $(n\lambda^3)$. For a hard-sphere diameter $a$, $A_2 = \frac{2\pi}{3}(a/\lambda)^3$ (see [5] below), and the higher order $A_j$’s may be expressed as $A_j = \kappa(A_2)^{j-1}$, where $\kappa$ is a constant [1]. Substituting this in (3), we see that the interaction energy of the classical hard-sphere gas vanishes identically in each power of $(n\lambda^3)$. In fact, the classical hard-sphere gas is rather special, since the right hand side of [1] is independent of temperature.

We note that in the regime $(n\lambda^3) \ll 1$, the series [3] may be terminated after the first order term

$$\frac{E_{\text{int}}}{N} = 3\frac{\tau}{2} \left\{ (n\lambda^3) \left[ a_2 - \frac{2}{3}\tau \frac{da_2}{d\tau} \right] \right\}. \quad (4)$$

The classical second virial coefficient $A_2$ is given by [5]

$$A_2(\beta) = \frac{2\pi}{\lambda^3} \int_0^\infty dr \ r^2 \ (1 - \exp(-\beta V(r))), \quad (5)$$

where $\beta = 1/\tau$, and $V(r)$ is the interatomic two-body potential. The quantum second virial coefficient requires a knowledge of the bound-state and the continuum spectra.
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For a one-component quantum gas, \( b_2 = -a_2 \) is given by [5]

\[
b_2(\beta) = \sum_{l=0}^{\infty} (2l+1)b_2^{(l)}(\beta)
\]

\[
b_2^{(l)}(\beta) = \sqrt{2} \left[ \sum_n \exp(-E_{n,l}/\beta) + \frac{1}{\pi} \int_0^{\infty} \frac{dk}{k} \frac{\partial \delta_l}{\partial k} \exp\left(-\frac{\hbar^2 k^2 \beta}{m}\right) \right].
\]

In the above, \( E_{n,l} \)'s are the binding energies of the two-body bound states (absent in our problem), and \( \delta_l \) is the scattering phase shift in the \( l \)th partial wave. It is important to note that our (6) differs from the usual definition given for quantum gases in text books [5, 7]: the overall multiplicative factor in our case being \( \sqrt{2} \) rather than \( 2\sqrt{2} \).

The second virial coefficient, after all, is just the two-body partition function for relative motion, and for the Boltzmann case it has a factor \( 1/N! \), which explains why our factor is less by 2 for the two-body case. Our definition here is in agreement with the earlier authors [2, 3, 8] who considered the Boltzmann case.

2.2. Numerical comparison

We compare the classical second virial coefficient \( A_2 = \frac{2\pi}{3}(a/\lambda)^3 \) with its quantum counterpart \( -b_2 \) as defined by (6) for the hard-sphere gas. The phase shift \( \delta_l \) for hard-sphere scattering is given by [9]

\[
\tan \delta_l = j_l(ka)/n_l(ka),
\]

and a little algebra shows that

\[
\frac{d\delta_l}{dk} = -\frac{a}{(ka)^2} \frac{1}{j_l^2(ka) + n_l^2(ka)}.
\]

For a fixed \( a \), as one goes to higher temperatures (i.e., larger values of \( (a/\lambda) \)), more and more \( l \) values are needed to get convergence in the computed \( b_2^{(l)} \) using (6). For example, for \( (a/\lambda) = 2 \), convergence is obtained only when the sum extends to \( l_{\text{max}} = 33 \) [4]. This may be understood by noting that for small \( \beta \) (high temperature), the damping of the integrand from the gaussian is less effective, and higher values of the variable \( k \) are needed for the convergence. From impact parameter argument [10], the cut off \( l_{\text{max}} \simeq (ka) \) in the sum over \( l \) therefore also increases. In figure [I] we display the classical and quantum second virial coefficients \( (A_2 \text{ and } -b_2) \) as a function of \( (a/\lambda) \).

One expects the classical regime for \( (a/\lambda) \gg 1 \). As is clear from figure [I] however, the two remain very different even in the so called classical regime. This difference may be understood from semiclassical corrections, as we shall see in the next section. For a perfect Boltzmann gas, the energy per particle, \( E_0/N = \frac{3}{2} \tau \). In figure [2] we plot \( E_{\text{int}}/E_0 \) in units of \( (n\lambda^3) \). Recall that this this quantity is exactly zero classically for any value of \( (n\lambda^3) \). In figure [2] the interaction energy is calculated from [II] to first order in \( (n\lambda^3) \), using the virial coefficient \( (-b_2) \) given by [6]. The disagreement between the classical and the quantum values of the second virial coefficient, as also the interaction energy, keeps increasing for larger values of \( (a/\lambda) \). This, however, is misleading, as we see below.

\[\text{¶} \text{ The quantity } b_2 \text{ was calculated by first summing over } l \text{ and then integrating. We specified a minimum relative error in the integrand (or the sum) of } 10^{-3}.\]
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**Figure 1.** The quantum and classical second virial coefficient with semiclassical corrections (to be discussed later.) The lowest curve gives the classical second virial coefficient and semiclassical approximations approach the quantum mechanical curve for sufficiently large $\alpha/\lambda$.

**Figure 2.** The quantum and semi-classical approximations to the interaction energy in units of $n\lambda^3$. 
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For fixed $a$ and $n$, larger values of $(a/\lambda)$ imply smaller $(n\lambda^3)$, which actually decreases the pressure $P/(n\tau)$ in (1) and the energy ratio $E_{\text{int}}/E_0$ in magnitude.

To get a better feel for figure 2, note that the maximum density for close packing of the hard spheres [1] is $n_{\text{max}} = \sqrt{2}/a^3$. In a dilute gas, let us assume that $n = n_{\text{max}}/10 = \sqrt{2}/(10a^3)$. We then get

$$\left(\frac{a}{\lambda}\right)^3 = \frac{\sqrt{2}}{10(n\lambda^3)}. \quad (8)$$

If we assume $(n\lambda^3) = 0.1$, we get $(a/\lambda)^3 = \sqrt{2}$, or $a/\lambda \approx 1$. From figure 2, we see that $E_{\text{int}}/E_0 \approx 0.12$ in this case as opposed to zero if this was calculated classically. Semiclassical corrections, to be discussed later, are still important in this regime. On the other hand, for a gas at equilibrium at room temperature and pressure, $n\lambda^3$ is at least ten times less, so quantum corrections are negligible.

In figure 3, we similarly plot $C_{\text{int}}/C_0$ in units of $(n\lambda^3)$ as a function of $(a\lambda)$.

**Figure 3.** The specific heat calculated quantum mechanically and using semi-classical approximations. Since the second term in the semi-classical expansion is zero, the one-term and two-term approximations are identical.

Classically, of course, $C_0$ is $3/2$ per particle in units of the Boltzmann constant, and $C_{\text{int}} = 0$.

### 3. The second virial coefficient

#### 3.1. The classical-quantum connection

In this section, the connection between the classical $A_2(\beta)$ and its quantum counterpart $-b_2(\beta)$ will be explored for a given two-body potential $V(r)$. This will help us to
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understand why the classical and quantum results are so different for the example that we are studying. For this purpose, it is convenient to make the partial wave decomposition

$$\mathcal{A}_2(\beta) = \frac{2\pi}{3} \left( \frac{\Lambda}{a} \right)^3 = \sum_{l=0}^{\infty} (2l+1) \mathcal{A}_2^{(l)} \cdot \tag{9}$$

it may be verified easily (by replacing the sum over $l$ by an integral), that

$$\mathcal{A}_2^{(l)} = \frac{1}{\lambda} \int_0^\infty dr \, \exp \left[ -\frac{\hbar^2 l(l+1)}{mr^2} \beta \right] \left[ 1 - \exp(-\beta V(r)) \right] . \tag{10}$$

One may enquire about the relation between this expression (10) and the quantum counterpart $b_2^{(l)}$. This question was actually answered nearly seventy years back by Kahn [11] in his doctoral dissertation. We shall give here a new compact derivation of his result, considering only the part of the virial coefficient arising from the scattering channel in the continuum. Using (6), and the relation $E = \frac{\hbar^2 k^2}{m}$, we have (with no bound states)

$$b_2^{(l)}(\beta) = \sqrt{2} \left[ \frac{1}{\pi} \int_0^\infty dE \, \frac{\partial \delta_l}{\partial E} \exp(-\beta E) \right] . \tag{11}$$

We note that $\frac{1}{\sqrt{2}} b_2^{(l)}(\beta)$ is just the Laplace transform of the derivative of the phase shift with respect to the energy. In the lowest order WKB approximation, the phase shift is given by [10]

$$[\delta_l(E)]_{\text{WKB}} = \sqrt{\frac{m}{\hbar^2}} \left[ \left( \int_{r_l}^\infty \sqrt{E - V_l(r)} - \int_{r_0}^{\infty} \sqrt{E - \frac{\hbar^2 l(l+1)}{mr^2}} \right) dr \right] . \tag{12}$$

In the above, the effective potential $V_l(r)$ is defined as

$$V_l(r) = V(r) + \frac{\hbar^2 l(l+1)}{mr^2} . \tag{13}$$

In (12), $r_l$ and $r_0$ are the classical turning points where the respective integrands go to zero. The derivative of the phase shift may be written as

$$\frac{[d\delta_l]}{dE}_{\text{WKB}} = \frac{1}{2} \sqrt{\frac{m}{\hbar^2}} \left[ \left( \int_0^\infty \Theta(E - V_l(r)) - \int_0^{\infty} \frac{\Theta(E - \frac{\hbar^2 l(l+1)}{mr^2})}{\sqrt{E - \frac{\hbar^2 l(l+1)}{mr^2}}} dr \right) \right] \tag{14}$$

in terms of the unit step function $\Theta(x)$. By noting that the Laplace transform of $\frac{\Theta(E - \mu)}{\sqrt{E - \mu}}$ is $\sqrt{\frac{\pi}{\beta}} \exp(-\beta \mu)$, we immediately obtain the desired result

$$\frac{1}{\sqrt{2}} b_2^{(l)}_{\text{WKB}} = -\frac{1}{\sqrt{2} \lambda} \int_0^\infty dr \, \exp \left[ -\frac{\hbar^2 l(l+1)}{mr^2} \right] [1 - \exp(-\beta V(r))]$$

$$= -\frac{\mathcal{A}_2^{(l)}}{\sqrt{2}} . \tag{15}$$
If the lowest order WKB approximation (14) for a given potential were exact, the classical and quantum (partial wave) virial coefficients would be the same. In general, of course, there are higher order semiclassical corrections in powers of $\hbar$ to the WKB lowest order term that accounts for the deviation from the classical result. We next examine the semiclassical corrections.

### 3.2. Semiclassical corrections to $A_2(\beta)$

There is the Wigner-Kirkwood [12, 13, 14] semiclassical expansion of the quantum partition function (or the second virial coefficient) in powers of $\hbar^2$ and the derivatives of the potential. This, however, is not applicable for the hard-sphere potential, since its derivatives do not exist. For the hard-sphere problem Hill [2] and Gibson [3] used advanced techniques in scattering theory to obtain the following asymptotic expansion for the virial coefficient:

$$b_2 = A_2 \left[ 1 + \frac{3}{2\sqrt{2}} \left( \frac{\lambda}{a} \right) + \frac{1}{\pi} \left( \frac{\lambda}{a} \right)^2 + \frac{1}{16\pi\sqrt{2}} \left( \frac{\lambda}{a} \right)^3 - \frac{1}{105\pi^2} \left( \frac{\lambda}{a} \right)^4 + \frac{1}{640\pi^2\sqrt{2}} \left( \frac{\lambda}{a} \right)^5 + O \left( \left( \frac{\lambda}{a} \right)^6 \right) \right],$$

(16)

where the classical virial coefficient $A_2 = \frac{2\pi^2}{3}(a/\lambda)^3$. Since $\lambda$ is proportional to $\hbar$, the above series is in powers of $\hbar$, and not $\hbar^2$. This is characteristic of potentials with sharp surfaces [8]. The derivation of the above series is quite involved, and will not be given here. We can present, however, a qualitative argument to indicate why one may expect powers of $(\lambda/a)$ in the semiclassical series above. Consider the integral (5) for $A_2(\beta)$ for the hard spheres. The potential $V(r)$ is zero whenever the relative distance $r$ between the centers of the spheres is greater than $a$. For $r = a$ the spheres touch each other with their sharp surfaces. Semiclassically, though, we may expect a fuzziness (or uncertainty) in the contact distance by an amount which is of the order of the de Broglie wavelength $\lambda_d = \hbar/\langle p \rangle$, where $p$ is the absolute value of the relative momentum between the two spheres. The average $\langle p \rangle$ with Boltzmann distribution, and the corresponding de Broglie wavelength are given by

$$\langle p \rangle = \frac{\int_0^\infty p^3 \exp(-p^2\beta/m)dp}{\int_0^\infty p^2 \exp(-p^2\beta/m)dp} = \frac{2}{\sqrt{\pi}} \frac{m}{\beta}, \quad \lambda_d = \frac{\lambda}{2\sqrt{2}}.$$

(17)

In evaluating the integral (5) semiclassically, we may put $V(r) = 0$ for $r \geq (a + \lambda_d)$, so that now the second virial coefficient becomes $\frac{2\pi}{3}(a + \lambda_d)^3/\lambda^3$. This may be written in the form of a series in powers of $(\lambda/a)$, multiplied by the classical term. This series, unlike the one given by (16), terminates with the cubic term. Although the coefficient of the leading $(\lambda/a)$ term is correctly reproduced, the agreement is fortuitous. The main merit of this derivation is simply to show that it is not unreasonable to expect semiclassical corrections in powers of $(\lambda/a)$. 


The order by order semiclassical corrections using (16) are computed and shown for the second virial coefficient (figure 1), the ratio of $E_{\text{int}}/E_0$ (figure 2), and the specific heat ratio $C_{\text{int}}/C_0$ (figure 3). We see from these that the semiclassical corrections are able to reproduce the quantum behaviour very well for $(a/\lambda) > 0.2$. Since the series (16) is an asymptotic one, the higher order terms are seen to diverge for small values of $(a/\lambda)$. Nonetheless, the series is very accurate for large values of $(a/\lambda)$. For a given $(a/\lambda)$, the asymptotic series under consideration has to be terminated after an optimum number of terms are summed.

We have thus demonstrated the usefulness of the semiclassical series for understanding the classical to quantum behaviour.

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**References**

[1] Hecht C E 1998 *Statistical thermodynamics and kinetic theory* (New York: Dover Publications)
[2] Hill R N 1968 *J. Math. Phys.* 9(10) 1534–1547
[3] Gibson W G 1970 *Phys. Rev. A* 2(3) 996–1002
[4] Beth E and Uhlenbeck G E 1937 *Physica* 4 915
[5] Pathria R K 1972 *Statistical mechanics* (Oxford: Pergamon Press) chap 9
[6] Ho T L and Mueller E J 2004 *Phys. Rev. Lett.* 92 160404+4
[7] Huang K 1965 *Statistical mechanics* (New York: John Wiley) See equation (14.67)
[8] DeWitt H E 1962 *J. Math. Phys.* 3 1003
[9] Flügge S 1974 *Practical Quantum Mechanics* (New York: Springer-Verlag) p 289
[10] Messiah A 1961 *Quantum mechanics* (North Holland) p 395
[11] Kahn B 1938 Ph.D. thesis University of Utrecht reproduced by De Boer J and Uhlenbeck G E eds 1965 in *Studies in Statistical Mechanics* vol 3 (Amsterdam: North Holland) p 281
[12] Wigner E 1932 *Phys. Rev.* 40(5) 749–759
[13] Kirkwood J G 1933 *Phys. Rev.* 44(1) 31–37
[14] Brack M and Bhaduri R K 2003 *Semiclassical physics* (Colorado: Westview Press) chap 4