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First Quantum-Mechanical Correction to the Classical Viscosity Cross Section of Hard Spheres

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The classical and first quantum correction terms in a high-energy expansion of the viscosity cross section $Q^{(2)}$ for a Boltzmann gas of hard spheres is derived. The first correction is found to be proportional to $(1/k\sigma)^{4/3}$, which is a term nonanalytic in $\hbar$ (i.e., $\hbar^{4/3}$), and results from scattering near the edge of the sphere. A bound is established showing the remainder of the asymptotic series to be of $O[\ln(k\sigma)/(k\sigma)^2]$. This asymptotic formula is compared with calculations based on the exact phase-shift expressions and its range of validity is established. The next correction terms are deduced to be proportional to $(\ln k\sigma)/(k\sigma)^2$ and $1/(k\sigma)^2$ which involve $\hbar^2 \ln \hbar$ and $\hbar^2$, respectively.

INTRODUCTION

In both classical and quantum mechanics one can, in a first-order Chapman-Enskog approximation, express the density-independent part of the viscosity in terms of an integral involving a specialized two-body cross section $Q^{(2)}$. While the latter admits of an exact quantum-mechanical formulation in terms of phase shifts, it is by no means trivial to extract from it an asymptotic expansion valid for high energies having the classical result as the leading term. In fact, for the case of a gas subject to Lennard-Jones forces, the quantum-mechanical corrections to the classical answer are still a subject under discussion.[1]

The development of a high-energy expansion is important in that, by providing corrections to the classical expression for the viscosity of light gases, it establishes the domain of validity of the classical term and provides simple formulas valid for a wider range of temperature. It also enables one to check the numerical work involved in evaluating the phase-shift formulas. Finally, by removing the values of these known terms from numerical results, we might expect to find clues to the analytical character of the remaining quantum-mechanical effects.

In this paper we derive the first two terms (classical and first quantum correction) of an expansion, valid at high energies, for the Boltzmann part of the cross section $Q^{(2)}$ of a gas of hard spheres. (Similar analysis should be possible for the other $Q^{(n)}$'s.) For this simple potential we can express phase shifts analytically in terms of Hankel functions and derive our results by using uniform asymptotic expansions for these functions.

The procedure is very different from the WKB method which yields the corrections for the Lennard-Jones potential as a power series in $\hbar^2$.

The hard-sphere interaction has, of course, an infinite discontinuity. Drawing upon the results holding for the second virial coefficient,[2] we anticipated that this would result in a high-energy dependence for the viscosity cross section which would not be analytic in $\hbar^2$. This expectation, which we verify in this paper, was one of our major reasons for choosing this potential. Another reason for studying hard spheres is the ease with which it enables one to carry out wide ranging and highly accurate numerical calculations. In addition, the reduction in the number of parameters characterizing this potential leads to increased possibilities for deriving analytical expressions for the results.

ANALYSIS

For Boltzmann statistics, the phase-shift expression for $Q^{(2)}$ reads

$$Q^{(2)}(k)=\frac{4\pi}{k^2}\sum_{l=0}^{\infty}\frac{(l+1)(l+2)}{(2l+3)}\sin^2[\delta_{l+2}(k)-\delta_l(k)], \quad (1)$$

where $\delta_l(k)$ is the phase shift for wave number k and angular-momentum quantum number l, and the sum extends over all positive integers. For the case of hard spheres, the phase shift is given by the expression

$$\tan\delta_l(k\sigma)=J_{l+1/2}(k\sigma)/N_{l+1/2}(k\sigma) ,$$

where J and N are, respectively, the Bessel and Neumann functions of order $l+\frac{1}{2}$ and argument $k\sigma$ with σ being the hard-sphere diameter.

It was pointed out by Buckingham, Davies, and Gilles[3] that Eq. (1) in this case can be written in a much more tractable form which, when divided by the classical value for this cross section, $\frac{2}{3}\pi N\sigma^2$, is

$$Q^{*(2)}(x)=\frac{6}{x^8}\sum_{l=0}^{\infty}\frac{(l+1)(l+2)(2l+3)}{A_l^2(x)A_{l+2}^2(x)} . \quad (2)$$

Here $x=k\sigma$ and

$$A_l^2(x)=(\pi/2x)\left[J_{l+1/2}^2(x)+N_{l+1/2}^2(x)\right] .$$

Expressed in terms of Hankel functions $H_\nu^{(1)}(x)$ and $H_\nu^{(2)}(x)$, Eq. (2) becomes

$$Q^{*(2)}(x)=\frac{24}{\pi^2x^6}\sum_{l=0}^{\infty}\frac{(l+1)(l+2)(2l+3)}{H_{l+1/2}^{(1)}(x)H_{l+1/2}^{(2)}(x)H_{l+5/2}^{(1)}(x)H_{l+5/2}^{(2)}(x)} . \quad (3)$$

In examining this equation, one is led to ask how much of the structure embodied in it is necessary to yield the classical limit and the leading correction. Certainly, for example, we would expect that to obtain the classical answer we should be able to replace the sum over l by an integral. Other simplifications are possible as well, and we discuss this in detail in Appendix A. We show there that for the large x in which we are interested, we can approximate Eq. (3) as

$$Q^{*(2)}(x)=\frac{48}{\pi^2x^6}\int_0^\infty d\nu\,\frac{\nu^3}{[H_\nu^{(1)}(x)H_\nu^{(2)}(x)]^2}+O\left(\frac{1}{x^2}\right) . \quad (4)$$

We shall demonstrate that the integral term contains the classical limit and the first correction, and thus provides a correct and simple starting point for developing an asymptotic series valid at high energies.

We shall first show how one can obtain the classical expression. We note that for large order, the Hankel function possesses the asymptotic expansion[4]

$$\pi H_\nu^{(1)}(x)=\sqrt{2}\,(x^2-\nu^2)^{-1/4}\times\exp[i(x^2-\nu^2)^{1/2}+i\nu\sin^{-1}(\nu/x)]\exp[-i\tfrac{1}{2}\pi(\nu+\tfrac{1}{2})]\times\left(\sum_{m=0}^{M-1}2^m b_m\Gamma(m+\tfrac{1}{2})(-i)^m(x^2-\nu^2)^{-(1/2)m}+O(x^{-M})\right), \quad (5)$$

where $x>\nu>0$ and

$$b_0=1,\quad b_1=\tfrac{1}{8}-\tfrac{5}{24}(1-x^2/\nu^2)^{-1},\ldots .$$

The second Hankel function $H_\nu^{(2)}(x)$ for real ν and x is the complex conjugate of $H_\nu^{(1)}(x)$, so keeping only the leading term we find that, for $x>\nu$,

$$H_\nu^{(1)}(x)H_\nu^{(2)}(x)\sim(2/\pi)(x^2-\nu^2)^{-1/2} . \quad (6)$$

If we insert this in Eq. (4) and integrate from $\nu=0$ to $\nu=x$, we obtain

$$Q^{*(2)}(x)=\frac{48}{\pi^2x^6}\int_0^x d\nu\,\nu^3(\tfrac{1}{2}\pi x)^2\left[1-\left(\frac{\nu}{x}\right)^2\right]=1; \quad (7)$$

i.e., we recover the classical result. The range of integration can be understood by observing that in the classical limit

$$\frac{\nu^2}{x^2}=\frac{(l+\frac{3}{2})^2}{k^2\sigma^2}\approx\frac{b^2}{\sigma^2} ,$$

where b is the classical impact parameter, and thus the above integral corresponds to those collisions for which the impact parameter does not exceed the diameter of the sphere. That is, we have considered just the range of b which in classical mechanics would give a collision.

One would be tempted to conclude at this point that to obtain further corrections it would suffice merely to keep additional terms in the asymptotic developments of $H_\nu^{(1)}(x)$ and $H_\nu^{(2)}(x)$ and not only to integrate the resulting expressions from 0 to x, but to carry out the equivalent procedure from x to ∞ also. This is unfortunately not true. It can be seen by examining Eq. (5) that additional terms will introduce singularities at $x=\nu$ into the integrand of Eq. (4), and thus will decrease the range of its applicability. The range excluded, where b is near σ, turns out, as we shall see, to be just that range in which we are most interested. One is then driven to treat this transitional region using expansions involving Bessel functions of order $\frac{1}{3}$ (and $-\frac{1}{3}$) or Airy functions. The whole procedure becomes quite complicated.

Instead, we begin by subtracting the classical contribution from the integral in Eq. (4). We then use Langer's uniform asymptotic expansions[5] for the Hankel functions and proceed to a limit valid for large k in a way developed by Rubinow and Wu[6] in their study of the elastic scattering cross section of cylinders and spheres. This procedure will be found to yield the first correction term.

Setting $x^2/\nu^2-1=\omega^2$, the classical contribution [Eq. (7)] can be written as

$$Q^{*(2)}=(48/\pi^2x^6)\int_0^x d\nu\,\tfrac{1}{4}\pi^2\nu^5\omega^2\,. \tag{8}$$

We now break up the integral of Eq. (4) into two parts,

$$Q_<=1+\frac{48}{\pi^2x^6}\int_0^x d\nu\left(\frac{\nu^3}{[H_\nu^{(1)}(x)H_\nu^{(2)}(x)]^2}-\tfrac{1}{4}\pi^2\nu^5\omega^2\right), \tag{9a}$$

$$Q_>=\frac{48}{\pi^2x^6}\int_x^\infty d\nu\,\frac{\nu^3}{[H_\nu^{(1)}(x)H_\nu^{(2)}(x)]^2}\,, \tag{9b}$$

where in $Q_<$ we have made use of Eq. (8).

We examine Eq. (9a) first. This corresponds to integrating over classical impact parameters less than the sphere radius. We use the uniform asymptotic expansions of Langer suitable for $x>\nu$:

$$H_\nu^{(1)}(x)=\omega^{-1/2}(\omega-\tan^{-1}\omega)^{1/2}H_{1/3}^{(1)}(z)\,e^{i\pi/6}+O(\nu^{-4/3})\,,$$
$$H_\nu^{(2)}(x)=\omega^{-1/2}(\omega-\tan^{-1}\omega)^{1/2}H_{1/3}^{(2)}(z)\,e^{-i\pi/6}+O(\nu^{-4/3})\,, \tag{10}$$

where $z=\nu(\omega-\tan^{-1}\omega)$. Equation (9a) therefore becomes, keeping only the lowest-order term,

$$Q_<=1+\frac{48}{\pi^2x^6}\int_0^x d\nu\,\nu^5\omega^2\left(\frac{1}{z^2[H_{1/3}^{(1)}(z)H_{1/3}^{(2)}(z)]^2}-\frac{\pi^2}{4}\right) \tag{11}$$

or

$$Q_<=1+\frac{48}{\pi^2x^2}\int_0^x dz\,\frac{\omega^2}{\tan^{-1}\omega}\,\frac{1}{(1+\omega^2)^2}\,\frac{1}{\omega-\tan^{-1}\omega}\times z\left(\frac{1}{z^2[H_{1/3}^{(1)}(z)H_{1/3}^{(2)}(z)]^2}-\frac{\pi^2}{4}\right). \tag{12}$$

For large x, and fixed z, ω becomes small since

$$z=[x/(1+\omega^2)^{1/2}](\omega-\tan^{-1}\omega)\,.$$

Thus, for $\omega^2<1$,

$$\frac{\omega^2}{\tan^{-1}\omega}\,\frac{1}{(1+\omega^2)^2}\,\frac{1}{\omega-\tan^{-1}\omega}\approx\frac{3}{\omega^2}\approx 3\left(\frac{x}{3z}\right)^{2/3} \tag{13}$$

and, if we make this approximation for all z, Eq. (12) becomes

$$Q_<=1+\frac{48}{\pi^2x^{4/3}}(3^{1/3})\times\int_0^\infty dz\,z^{1/3}\left(\frac{1}{z^2[H_{1/3}^{(1)}(z)H_{1/3}^{(2)}(z)]^2}-\frac{\pi^2}{4}\right), \tag{14}$$

where we have also let the upper limit x, which we assumed to be large, go to ∞.

We shall now show that Eq. (14), obtained by keeping ω small while letting $x\to\infty$, is correct to order $1/x^2$. Consider first the error resulting from letting ω become small:

$$E_1=\frac{48}{\pi^2x^2}\int_0^x dz\left[\frac{3}{\omega^2}-\frac{\omega^2}{(\tan^{-1}\omega)(1+\omega^2)^2(\omega-\tan^{-1}\omega)}\right]\times\left|z\left(\frac{1}{z^2[H_{1/3}^{(1)}(z)H_{1/3}^{(2)}(z)]^2}-\frac{\pi^2}{4}\right)\right|. \tag{15}$$

Note that we take the absolute value of the terms which are explicitly z dependent. Also, if we call the factor within the large square brackets (which contains the terms explicitly ω dependent) $G(\omega)$; then $G(\omega)$ is ≥ 0. This is shown simply by noting the following upper and lower bounds:

$$\omega/(1+\omega^2)<\tan^{-1}\omega<\omega\,, \tag{16a}$$

$$\tfrac{1}{3}\omega^3/(1+\omega^2)<\omega-\tan^1\omega<\tfrac{1}{3}\omega^3\,. \tag{16b}$$

Equation (16a) can be verified for all values of ω from the well-known expansions of[7] $\tan^{-1}\omega$ while Eq. (16b) can be shown to hold when ω is small. One can then extend the validity of (16b) to all values of ω by noting that the differences in the slopes of the terms are always positive.

Since we have

$$G(\omega)=\frac{3(\tan^{-1}\omega)(1+\omega^2)^2(\omega-\tan^{-1}\omega)-\omega^4}{\omega^2(\tan^{-1}\omega)(1+\omega^2)^2(\omega-\tan^{-1}\omega)}, \tag{17}$$

we can expand the square in the numerator, use the upper bound given by (16b) on the first term, and group the results to yield

$$G(\omega)\le\frac{3(\tan^{-1}\omega)\frac{1}{3}\omega^3-\omega^4}{\omega^2(\tan^{-1}\omega)(1+\omega^2)^2(\omega-\tan^{-1}\omega)}+\frac{3(2+\omega^2)}{(1+\omega^2)^2}\ .$$

The first term here will vanish after applying the appropriate bounds leaving

$$G(\omega)\le\frac{3}{(1+\omega^2)^2}+\frac{3}{1+\omega^2}\ . \tag{18}$$

For large z, Hankel's asymptotic expansion[8] gives

$$\frac{1}{z^2[H^{(1)}_{1/3}(z)H^{(2)}_{1/3}(z)]^2}-\frac{\pi^2}{4}\sim\frac{c}{z^2}\ , \tag{19}$$

where c is a constant, and thus, inserting Eqs. (18) and (19) in (15), we obtain

$$E_1\le O\left(\frac{\ln x}{x^2}\right)=O\left(\frac{1}{x^2}\right)\ .$$

The error in $Q_<$ due to neglecting the terms of $O(\nu^{-4/3})$ of Eq. (10) in arriving at Eq. (11) is evaluated in Appendix B and is shown there to also be of $O(1/x^2)$.

We next consider the effect of extending the upper limit to infinity in Eq. (14), and hence we must estimate

$$E_2=\frac{48(3^{1/3})}{\pi^2x^{4/3}}\int_x^\infty dz\,z^{1/3}\left(\frac{1}{z^2[H^{(1)}_{1/3}(z)H^{(2)}_{1/3}(z)]^2}-\frac{\pi^2}{4}\right)\ . \tag{20}$$

Using (19) we see that the integrand goes as $z^{-5/3}$, and thus E_2 is $O(1/x^2)$.

This analysis, of course, also shows that the integral of Eq. (14) converges at the upper limit. For small z, from the power-series expansion of the Hankel functions,[9] we obtain

$$\frac{1}{z^2[H^{(1)}_{1/3}(z)H^{(2)}_{1/3}(z)]^2}\sim\frac{1}{\frac{1}{3}z^2}\ . \tag{21}$$

Thus the integrand near the origin behaves as $z^{-1/3}$ which poses no problem, and we have completed our analysis of Eq. (9a), showing that we can replace it by Eq. (14) with errors no greater than $O(1/x^2)$.

We now turn to Eq. (9b), which corresponds to integrating over impact parameters larger than the sphere radius, and proceed in an analogous fashion. For $x<\nu$, the asymptotic expansions of Langer are

$$H^{(1)}_\nu(x)=\omega^{-1/2}(\tanh^{-1}\omega-\omega)^{1/2}\times\{(1/\pi)K_{1/3}(z)-i[I_{1/3}(z)+I_{-1/3}(z)]\}+O(\nu^{-4/3})\ ,$$

$$H^{(2)}_\nu(x)=\omega^{-1/2}(\tanh^{-1}\omega-\omega)^{1/2}\times\{(1/\pi)K_{1/3}(z)+i[I_{1/3}(z)+I_{-1/3}(z)]\}+O(\nu^{-4/3})\ , \tag{22}$$

where now $\omega^2=1-x^2/\nu^2$ and $z=\nu(\tanh^{-1}\omega-\omega)$. Equation (9b) then takes the form

$$Q_>=\frac{48}{\pi^2x^6}\int_x^\infty d\nu\,\nu^3\frac{\omega^2}{(\tanh^{-1}\omega-\omega)^2}\times\frac{1}{\{[(1/\pi)K_{1/3}(z)]^2+[I_{1/3}(z)+I_{-1/3}(z)]^2\}^2}$$
$$=\frac{48}{\pi^2x^2}\int_0^\infty dz\,\frac{\omega^2}{\tanh^{-1}\omega}\,\frac{1}{(1-\omega^2)^2}\,\frac{1}{(\tanh^{-1}\omega-\omega)}\times\frac{1}{z\{[(1/\pi)K_{1/3}(z)]^2+[I_{1/3}(z)+I_{-1/3}(z)]^2\}^2}\ , \tag{23}$$

where we have neglected the terms $O(\nu^{-4/3})$ which could be treated in a manner analogous to that used in Appendix B. If we again take the limit $x\to\infty$, then, for fixed z,ω again is small and

$$\frac{\omega^2}{\tanh^{-1}\omega}\,\frac{1}{(1-\omega^2)^2}\,\frac{1}{(\tanh^{-1}\omega-\omega)}\sim\frac{3}{\omega^2}\ , \tag{24a}$$

which, as before, becomes

$$3/\omega^2\sim3(x/3z)^{2/3}=3^{1/3}x^{2/3}z^{-2/3}\ . \tag{24b}$$

If we now approximate the integrand of $Q_>$ in this manner, we find

$$Q_>=\frac{48}{\pi^2}\,\frac{1}{x^{4/3}}\,3^{1/3}\times\int_0^\infty dz\,\frac{z^{-5/3}}{\{[(1/\pi)K_{1/3}(z)]^2+[I_{1/3}(z)+I_{-1/3}(z)]^2\}^2} \tag{25}$$

for large x. For small z the integrand behaves as $z^{-1/3}$, and for large z the integrand decreases exponentially.

As before we can write an upper bound for the error that we have committed by keeping ω small. Using the following bounds, which can be verified by arguments analogous to those used for Eqs. (16):

$$\omega/(1-\omega^2)>\tanh^{-1}\omega>\omega,$$
$$\omega^3/3(1-\omega^2)>\tanh^{-1}\omega-\omega>\tfrac{1}{3}\omega^3\ , \tag{26}$$

we find that

$$3\left(\frac{1}{(1-\omega^2)^2}+\frac{1}{1-\omega^2}\right)>\frac{\omega^2}{\tanh^{-1}\omega}\,\frac{1}{(1-\omega^2)^2}\,\frac{1}{\tanh^{-1}\omega-\omega}-\frac{3}{\omega^2}>0\ . \tag{27}$$

Thus the error introduced in going from Eq. (23) to (25) is

$$E_3 < \frac{48}{\pi^2 x^2} \times 3 \int_0^\infty dz \left(\frac{1}{(1-\omega^2)^2} + \frac{1}{(1-\omega^2)} \right) \times \frac{1}{z} \frac{1}{\{(1/\pi) K_{1/3}(z)^2 + [I_{1/3}(z) + I_{-1/3}(z)]^2\}^2} . \quad (28)$$

To estimate this expression, we note that the integrand decreases exponentially ($\sim e^{-4z}$) for large z. Since we are interested in the large x behavior, we let ω approach zero as we did before. This removes the x dependence from the integral and the upper limit of the error E_3 is of order $1/x^2$.

Our result is then

$$Q^{*(2)}(x) = 1 + (A + B) x^{-4/3} + O(1/x^2) , \quad (29)$$

where

$$A = \frac{48}{\pi^2} 3^{1/3} \int_0^\infty dz\, z^{1/3} \left(\frac{1}{z^2 [H_{1/3}^{(1)}(z) H_{1/3}^{(2)}(z)]^2} - \tfrac{1}{4}\pi^2 \right) , \quad (30a)$$

$$B = \frac{48}{\pi^2} 3^{1/3} \int_0^\infty dz\, z^{-5/3} \times \frac{1}{\{[(1/\pi) K_{1/3}(z)]^2 + [I_{1/3}(z) + I_{-1/3}(z)]^2\}^2} . \quad (30b)$$

The first quantum correction term has thus been obtained by finding limiting values for the integrals when x is large and ω remains small. Since the quantity ω is a relative measure of the deviation of the classical impact parameter from the sphere radius, we see that the first quantum correction results from picking out for each energy those angular momenta which result in collisions where the impact parameter is near the sphere radius. The coefficient A embodies a contribution in excess of the classical term from just inside the sphere, while B gives a contribution from just outside it.

CALCULATIONS

The next step is to evaluate the integrals associated with the coefficients A and B given by Eq. (30). Numerical integration was used to accomplish this, and a few comments are in order on the procedure we have followed.

From a numerical point of view the A integral presents the following difficulties: (a) Its integrand is proportional to $z^{-1/3}$ near the origin; (b) for large z the convergence is slow; and (c) we must produce accurate values of the Hankel functions. To deal with these problems we split the integration into three regions: 0 to 1, 1 to x, and x to ∞. For the first region we change variables, letting $z^{1/3} = u$. The change of variables is suggested by the behavior of the integrand which now becomes linear in u and thus presents no difficulty. To evaluate the Hankel functions in regions one and two, we rewrite the product in terms of positive fractional order Bessel functions,

$$H_{1/3}^{(1)}(z) H_{1/3}^{(2)} = [J_{1/3}(z)]^2 + \tfrac{1}{3}[J_{1/3}(z) + 2J_{5/3}(z) - \tfrac{8}{3}(1/x) J_{2/3}(z)]^2 \quad (31)$$

and evaluate these by backward recursion.[10] Finally, to evaluate the third region we use Hankel's asymptotic series[8] for $|z| \gg 1$, $|z| \gg \nu$, and we obtain

$$\left(\frac{1}{z^2 [H_{1/3}^{(1)}(z) H_{1/3}^{(2)}(z)]^2} - \frac{\pi^2}{4} \right) = \frac{\pi^2}{4} \left(\frac{5}{36} \right) \frac{1}{z^2} \left(1 - \frac{3}{2z^2} + \cdots \right) . \quad (32)$$

We can then integrate Eq. (30a) from an arbitrary large value of z $(=x)$ to ∞. Calling this contribution the "tail," we find

$$\text{tail} = \tfrac{5}{2} \times 3^{1/3} (1/x^{2/3})(1 - 3/8x^2 + \cdots) . \quad (33)$$

In our evaluation we let $x = 40.5$.

Our value for A is then the sum of three numbers: 4.332027, 2.748426, and 0.305664, so $A = 7.386117 \pm 0.000001$ (or 2).

The B integral is treated similarly except that owing to the exponential convergence of the integrand there is no need for a third region. By $z = 6$ the integral of the second region has converged to eight figures and represents only a small fraction of the contribution of the first region. We find then that $B = 2.990688$. Thus $A + B = 10.376805 \pm 0.000001$ (or 2), and we have the final result

$$Q^{*(2)}(x) = 1 + 10.376805\, x^{-4/3} + O(1/x^2) . \quad (34)$$

This contrasts with a dependence of $x^{-2/3}$ for the first correction to the scattering cross section for hard spheres (we recall that the leading term is twice the classical value) and contrasts with an expansion in powers of $1/x$ for the derivative of the second-virial-coefficient phase-shift sum for hard spheres.

Equation (34) has been compared with 15 digit calculations of this cross section from Eqs. (1) and (2), and the results are displayed in Fig. 1. Good numerical agreement is attained at large values of x. For example, Eq. (34) gives values which are only 0.55% too high at $x = 100$, 0.1% too high at $x = 1000$, and 0.001% too high at $x = 4000$.

A comparison of the deviations from the classical values, $Q^{*(2)}(x) - 1$, provides a more sensi-

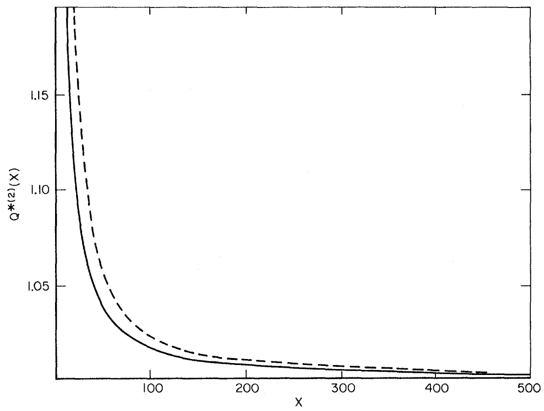

FIG. 1. $Q^{*(2)}(x)$; solid line, calculated by the exact phase-shift formula, Eq. (2); dot-dash line calculated by the two-term asymtotic formula, Eq. (33).

tive test of the adequacy of Eq. (34) for representing the large-x behavior. We find that it gives a value which is too high by less than 10% at $x \sim 900$, and within 5% at about 3500. The slope of the actual deviation on a log-log plot does not come within 1% of $-\frac{4}{3}$ until after $x \approx 2500$. This indicates a slow rate of convergence for the asymptotic series which has been borne out by fittings to a semi-empirical series suggested by this work. This has been carried out over a range from $x = 30$ to 4200 and gives a value of 10.376 805 5 with an estimated error of $\pm 0.000\,000\,2$ for the coefficient of $x^{-4/3}$, thus verifying the result derived in this paper quite convincingly. In addition, the error estimates obtained here for the neglected quantities indicate that the next terms in the asymptotic series should be proportional to $(\ln x)/x^2$ and $1/x^2$. These terms are supported by the least-squares analysis of the phase-shift calculations, and preliminary fittings indicate values of about -17.000 and $+25.149$, respectively, for their coefficients. More accurate fittings, including higher terms, will be published separately together with the exact calculations.

We wish to emphasize that Eq. (34) and its semi-empirical extension, including as they do both fractional powers of the energy and logarithmic behavior, are not analytic in $\hbar^2$, nor in $\hbar$, as was the case with the second virial coefficient of hard spheres. This raises the possibility that non-analyticities may also be present in the asymptotic expansion of the transport cross sections for more realistic potentials.

APPENDIX A

We wish to show that when x is large, we can write the reduced-viscosity cross section for hard spheres to order $1/x^2$ as

$$Q^{*(2)}(x) = \frac{48}{\pi^2}\,\frac{1}{x^6}\int_0^\infty d\nu\,\frac{\nu^3}{[H_\nu^{(1)}(x)H_\nu^{(2)}(x)]^2}\;. \quad \text{(A1)}$$

We start from the rigorous expression

$$Q^{*(2)} = \frac{24}{\pi^2 x^6} \times \sum_{l=0}^{\infty} \frac{(l+1)(l+2)(2l+3)}{H_{l+1/2}^{(1)}(x)\,H_{l+1/2}^{(2)}(x)\,H_{l+5/2}^{(1)}(x)\,H_{l+5/2}^{(2)}(x)}\;. \quad \text{(A2)}$$

Let $\nu = l + \frac{3}{2}$. Then we have

$$Q^{*(2)} = \frac{48}{\pi^2 x^6}\sum_{\nu=3/2}^{\infty}\frac{\nu^3}{H_{\nu-1}^{(1)}(x)\,H_{\nu-1}^{(2)}(x)\,H_{\nu+1}^{(1)}(x)\,H_{\nu+1}^{(2)}(x)} - \frac{12}{\pi^2 x^6}\sum_{\nu=3/2}^{\infty}\frac{\nu}{H_{\nu-1}^{(1)}(x)\,H_{\nu-1}^{(2)}(x)\,H_{\nu+1}^{(1)}(x)\,H_{\nu+1}^{(2)}(x)}\;, \quad \text{(A3)}$$

where the sum goes over odd half-integral values.

We begin by examining the first of the sums in Eq. (A3), and we replace it by an integral using the Euler-Maclaurin expansion[11]:

$$Q^{*(2)} = \frac{48}{\pi^2 x^6}\left(\int_{3/2}^{\infty} dn\,F(n) + \tfrac{1}{2}[F(\infty) + F(\tfrac{3}{2})] + \sum_{m=1}^{\infty}\frac{1}{(2m)!}\,B_m[F^{(2m-1)}(\infty) - F^{(2m-1)}(\tfrac{3}{2})]\right), \quad \text{(A4)}$$

where

$$F(n) = n^3/[H_{n-1}^{(1)}(x)\,H_{n-1}^{(2)}(x)\,H_{n+1}^{(1)}(x)\,H_{n+1}^{(2)}(x)]\;,$$

the B_m's are Bernoulli numbers, and the $F^{(2m-1)}$'s are derivatives of F with respect to n. Our next step will be to replace the differing orders of the Hankel functions by their average value n and to examine the error E_4 introduced by this approximation:

$$E_4 = \frac{48}{\pi^2 x^6}\left(\int_{3/2}^{\infty} dn\,\frac{n^3}{H_{n-1}^{(1)}(x)\,H_{n-1}^{(2)}(x)\,H_{n+1}^{(1)}(x)\,H_{n+1}^{(2)}(x)} - \int_{3/2}^{\infty} dn\,\frac{n^3}{[H_n^{(1)}(x)H_n^{(2)}(x)]^2}\right). \quad \text{(A5)}$$

We estimate this error using the expansions for Hankel functions of large order, and consider first the lower part of the integrals (which we designate $E_{4<}$), where $x > \nu > 0$.

The expansion (Eq. 5)

$$\frac{1}{H_\nu^{(1)}(x)H_\nu^{(2)}(x)} \approx \tfrac{1}{2}\pi(x^2-\nu^2)^{1/2}\left[1 + O\left(\frac{1}{x^2}\right)\right] \quad \text{(A6)}$$

gives us

$$\frac{1}{[H_n^{(1)}(x)H_n^{(2)}(x)]^2}=\frac{\pi^2x^2}{4}\left(1-\frac{n^2}{x^2}\right)\left[1+O\left(\frac{1}{x^2}\right)\right],$$

$$\frac{1}{H_{n+1}^{(1)}(x)H_{n+1}^{(2)}(x)H_{n-1}^{(1)}(x)H_{n-1}^{(2)}(x)}\approx\frac{\pi^2x^2}{4}\left[1-\left(\frac{n+1}{x}\right)2\right]^{1/2}\times\left[1-\left(\frac{n-1}{x}\right)2\right]^{1/2}\left[1+O\left(\frac{1}{x^2}\right)\right]^2$$

$$\approx\frac{\pi^2x^2}{4}\left(1-\frac{n^2}{x^2}\right)\left[1+O\left(\frac{1}{x^2}\right)\right]. \quad \text{(A7)}$$

Inserting in Eq. (A5) and integrating from $\frac{3}{2}$ to x gives the result

$$E_{4<}=O(1/x^2)\ . \quad \text{(A8)}$$

For the upper part of our error integral equation (A5), where we integrate from x to ∞, we use the expansion for $\nu>x>0$,[4]

$$H_\nu^{(1)}(x)H_\nu^{(2)}(x)\approx\frac{2}{\pi^2(\nu^2-x^2)^{1/2}}\times\exp\{2\nu[-(1-x^2/\nu^2)^{1/2}+\cosh^{-1}(\nu/x)]\}\times\left(\sum_{m=0}(-1)^m\frac{a_m}{(\nu^2-x^2)^{m/2}}\right)^2, \quad \text{(A9)}$$

where $a_m=2^m\Gamma(m+\frac{1}{2})\,b_m$ and the b_m are the same as in Eq. (5).

The argument of the exponential is always positive in our range of integration. This is easily seen by noting that both terms in the bracket are zero at $\nu=x$, while the slope of the positive $\cosh^{-1}(\nu/x)$ term with increasing ν is always steeper than that of the negative term. Thus in the error integral we have a decreasing exponential which goes to zero as $\nu\to\infty$.

We can get an upper bound to $E_{4>}$ by splitting it into a lower and an upper part. For the lower part of the range of integration ($E_{4>,e}$), we replace the exponential terms by their largest value 1, and integrate from x to a large upper limit b. We obtain

$$E_{4>,e}<\frac{48}{\pi^2x^6}\int_x^b dn\,n^3\,\frac{\pi^2}{4}\,O(1)\approx O\left(\frac{1}{x^2}\right). \quad \text{(A10)}$$

For the range from b to infinity ($E_{4>,u}$) we will designate the argument of the exponential as $-\nu f(\nu)$ and replace it by $-\nu f(b)$. We then obtain

$$E_{4>,u}<\frac{48}{\pi^2x^6}\int_b^\infty dn\,n^3\tfrac{1}{4}\pi^2(n^2-x^2)\left[1+O\left(\frac{1}{(n^2-x^2)^{1/2}}\right)\right]\times e^{-cn}(1-e^{-dn})\approx O\left(\frac{1}{x^4}\right). \quad \text{(A11)}$$

We have thus shown that we can replace the orders of the Hankel functions by their average values and keep the error $O(1/x^2)$.

We consider next the error introduced by allowing the lower limit of the error integral Eq. (A5) to go to zero. We can employ the expansion of the Hankel function when the argument is very large[8], and we have

$$E_5=\frac{48}{\pi^2x^6}\int_0^{3/2}dn\,\frac{n^3}{[H_n^{(1)}(x)H_n^{(2)}(x)]^2}\approx\frac{48}{\pi^2x^6}\,\frac{\pi^2x^2}{2^2}\int_0^{3/2}dn\,n^3=O\left(\frac{1}{x^4}\right). \quad \text{(A12)}$$

Thus we can drop the lower limit of our integral to zero and still retain the desired accuracy.

Next we must consider the values of $F(n)$ and its derivatives with respect to n at the two limits, as they appear in Eq. (A4).

At the lower limit we have $n\ll x$, since we are considering large values of x. In this case $H_n^{(1)}(x)\times H_n^{(2)}(x)\approx 2/(\pi x)$ so $F(\frac{3}{2})$ is of order x^2 and its contribution to $Q^{*(2)}(x)$ will be $O(1/x^4)$.

At the upper limit ∞, we have $n\gg x$, and in this case[12] we have

$$H_n^{(1)}(x)H_n^{(2)}(x)\approx(2n/x)^{2n}\ .$$

Hence, as $n\to\infty$, $F(n)\approx(x/2n)^{4n}$ which goes to zero very strongly as $n\to\infty$.

Thus $F(\infty)$, and indeed, all of its derivatives with respect to n will give no contribution to $Q^{*(2)}(x)$.

Our last step is now to examine the derivatives at the lower limit $n=\frac{3}{2}$. Let

$$F(n)=n^3/G(n-1)G(n+1)\ , \quad \text{(A13)}$$

where $G(n-1)=H_{n-1}^{(1)}(x)H_{n-1}^{(2)}(x)$, etc. Then

$$\frac{dF(n)}{dn}=\frac{3}{n}F(n)-F(n)\left(\frac{G'(n+1)}{G(n+1)}+\frac{G'(n-1)}{G(n-1)}\right), \quad \text{(A14)}$$

where G' is the derivative of G with respect to n. The first term on the right-hand side of Eq. (A14) is clearly of order $1/x^2$ lower than the order of $\int_a^x dn\,F(n)$ since we lose one power of x by dropping the integration over dn, and one in differentiating with respect to n.

To evaluate the second term in Eq. (A14) we again use the expansion [Eq. (5)], since $x\gg n$, and obtain

$$\frac{G'}{G} = \frac{1}{G}\frac{dG}{dn} \approx \frac{1}{(1-n^2/x^2)}\left(+\frac{n}{x^2}\right) .$$

Thus the second term of Eq. (A14) is of order $(1/x^2)$ lower than the order of $F(n)$, and of order $(1/x^3)$ lower than that of the integral over $F(n)$, and we can drop the terms involving the derivatives at the lower limit without introducing any errors greater than $O(1/x^2)$.

The analysis of the second sum in Eq. (A3) proceeds as for the first sum. Because of the appearance of ν instead of ν^3 the contributions from this term will be down by a factor of $1/x^2$ relative to those arising from the first sum and so this sum can be neglected.

We have thus shown that Eq. (A3) can be replaced by Eq. (A1) with errors no larger than order $(1/x^2)$.

APPENDIX B

The expressions of Langer for the Hankel functions [Eqs. (10)] are the initial terms of a uniform asymptotic expansion derived by Olver[5]:

$$H_\nu^{(1)}(\nu y) \sim 2e^{-i\pi/3}\left(\frac{4\xi}{1-y^2}\right)^{1/4}\left(\frac{\mathrm{Ai}(e^{2\pi i/3}\nu^{2/3}\xi)}{\nu^{1/3}}\sum_{k=0}^{\infty}\frac{a_k(\xi)}{\nu^{2k}} + e^{2\pi i/3}\,\frac{\mathrm{Ai}'(e^{2\pi i/3}\nu^{2/3}\xi)}{\nu^{5/3}}\sum_{k=0}^{\infty}\frac{b_k(\xi)}{\nu^{2k}}\right) . \tag{B1}$$

$H_\nu^{(2)}$ is the complex conjugate of this. For $y \geq 1$, our case, $(-\xi)^{3/2} = \frac{3}{2}[(y^2-1)^{1/2} - \cos^{-1}(1/y)]$, and the a_k's and b_k's are series in inverse fractional powers of ξ with $a_0 = 1$. Rewriting in our variables, x, z, and ω, one has

$$H_\nu^{(1)}(x) \simeq \frac{(\omega - \tan^{-1}\omega)^{1/2}}{\omega^{1/2}}\, H_{1/3}^{(1)}(z)\, e^{i\pi/6}\left(\sum_{k=0}^{\infty}\frac{a_k(\xi)}{\nu^{2k}}\right)\left[1 + \left(\frac{3}{2}\right)^{1/3}\frac{(\omega-\tan^{-1}\omega)^{4/3}}{z}\,\frac{H_{2/3}^{(1)}(z)}{H_{1/3}^{(1)}(z)}\,e^{-i\pi/3} \times\left(\sum_{k=0}^{\infty}\frac{b_k}{\nu^{2k}}\Big/\sum_{k=0}^{\infty}\frac{a_k(\xi)}{\nu^{2k}}\right)\right] \tag{B2}$$

and a similar expression for $H_\nu^{(2)}(x)$.

The square of their product thus becomes

$$[H_\nu^{(1)}(x)H_\nu^{(2)}(x)]^2 \sim \left(\frac{\omega-\tan^{-1}\omega}{\omega}\right)^2 H_{1/3}^{(1)}(z)H_{1/3}^{(2)}(z)\left(\sum_{k=0}^{\infty}\frac{a_k(\xi)}{\nu^{2k}}\right)^2\left\{1 + \left(\frac{3}{2}\right)^{1/3}\left(\frac{\omega-\tan^{-1}\omega}{z}\right)^{4/3} \times\left[\frac{H_{2/3}^{(1)}(z)e^{-i\pi/3}}{H_{1/3}^{(1)}(z)} + \frac{H_{2/3}^{(2)}(z)e^{i\pi/3}}{H_{1/3}^{(2)}(z)}\right]\left(\sum_{k=0}^{\infty}\frac{b_k}{\nu^{2k}}\Big/\sum_{k=0}^{\infty}\frac{a_k}{\nu^{2k}}\right) + O\left(\frac{1}{z^2}\right)\right\} . \tag{B3}$$

We shall first examine the terms in the summation over a_k/ν^{2k}. For $k=0$ we have $a_0/\nu^0 = 1$ and this term gives us Eq. (11) of the text. The next term, for $k=1$, is

$$\frac{a_1}{\nu^2} = \frac{1}{z^2}\left[\frac{(\omega-\tan^{-1}\omega)^2}{1152}\left(\frac{81}{\omega^2} + \frac{462}{\omega^4} + \frac{385}{\omega^6}\right) - \frac{14}{3(1152)}(\omega - \tan^{-1}\omega)\left(\frac{3}{\omega} + \frac{5}{\omega^3}\right) + \frac{455}{9(1152)}\right] . \tag{B4}$$

If we assume that ω is small as we did when examining the contribution of the first term in the series, Eq. (11), we can expand the $\omega - \tan^{-1}\omega$ terms in powers of ω, and we find that the coefficients of the first few powers occurring $(\omega^0, \omega^2, \omega^4)$ are identically zero. We can, therefore, neglect a_1/ν^2 (and higher-order terms) in the "a" sum.

The first term in the sum over b_k/ν^{2k} is

$$\frac{b_0}{\nu^0} = \frac{2^{1/3}}{3^{1/3}(\omega-\tan^{-1}\omega)^{1/3}}\left(-\frac{5}{72(\omega-\tan^{-1}\omega)} + \frac{5}{24\omega^3} + \frac{1}{8\omega}\right) , \tag{B5}$$

which, for small ω is

$$b_0/\nu^0 \approx (2^{1/3}/70)[1 - O(\omega^2)], \tag{B6}$$

and we can approximate this by the first term, a constant, and neglect higher terms in the summation.

Using these approximations for the sums, $\sum a_k/\nu^{2k} = 1$ and $\sum b_k/\nu^{2k} =$ constant, we next show that the second term in the curly brackets of Eq. (B3) becomes small compared to one when x is large. The quantity

$(\omega - \tan^{-1}\omega)^{4/3}/z$ can be written $z^{1/3}(1+\omega^2)^{2/3}/x^{4/3}$. Since ω remains less than 1 for even our largest values of $z=x$, this quantity is small compared to 1 and at least of order $(1/x)$.

The factor in the square brackets multiplying it can be shown to be bounded in our range of interest. At small values of z we can expand the Hankel functions by their series expressions and we find that the ratios go as $z^{-1/3}$. This is cancelled out by the factor $z^{1/3}$ in front, leaving the second term in curly brackets of order $1/x^{4/3}$. For large z, the square-bracket factor approaches zero, so the second term vanishes.

Since the second term in the curly bracket of Eq. (B3) is small compared to one, we can substitute Eq. (B3) in Eq. (9a) and expand the denominator.

This will give us Eq. (11) plus a correction from the higher-order terms neglected there:

$$E_6 = \frac{48}{\pi^2 x^2}\int_0^x dz\, \frac{\omega^2}{(\tan^{-1}\omega)(1+\omega^2)^2}\; \frac{z}{(\omega - \tan^{-1}\omega)z^2[H^{(1)}_{1/3}(z)H^{(2)}_{1/3}(z)]^2}$$
$$\times \left[-\frac{3^{1/3}}{70}\, \frac{(1+\omega^2)^{2/3} z^{1/3}}{x^{4/3}} \left(\frac{H^{(1)}_{2/3}(z)e^{-i\pi/3}}{H^{(1)}_{1/3}(z)} + \frac{H^{(2)}_{2/3}(z)e^{i\pi/3}}{H^{(2)}_{2/3}(z)} \right)\right] . \qquad \text{(B7)}$$

When ω is small, this becomes

$$E_6 = \frac{-48\times 3^{2/3}}{70\pi^2 x^{8/3}}\int_0^x dz\, z^{2/3}\, \frac{1}{z^2[H^{(1)}_{1/3}(z)H^{(2)}_{1/3}(z)]^2} \left(\frac{H^{(1)}_{2/3}(z)e^{-i\pi/3}}{H^{(1)}_{1/3}(z)} + \frac{H^{(2)}_{2/3}(z)e^{i\pi/3}}{H^{(2)}_{1/3}(z)} \right) . \qquad \text{(B8)}$$

We can obtain an upper limit for this error by using the large argument expansions of the Hankel functions[8] which gives us

$$E_6 \sim \frac{-48\times 3^{2/3}}{35\pi^2 x^{8/3}}\int_0^x dz\, z^{2/3}\, \frac{\pi^2}{4}\left(\frac{1}{12z}\right) = O\left(\frac{1}{x^2}\right) , \qquad \text{(B9)}$$

and we can thus neglect the higher-order terms in Eq. (10).

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[1]For a brief summary and references on this problem, see R. A. Buckingham and E. Gal, *Advances in Atomic and Molecular Physics*, edited by D. R. Bates and I. Estermann (Academic, New York, 1968), Vol. 4, p. 46.

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[5]See Ref. 4, p. 89. For higher-order terms see Ref. 7, p. 368.

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[7]*Handbook of Mathematical Functions*, edited by M. Abramowitz and I. A. Stegun, Natl. Bur. Std. (U.S.) Applied Math. Series No. 55 (U.S. GPO, Washington, D. C., 1964), p. 81.

[8]See Ref. 7, p. 364.

[9]See Ref. 7, p. 360.

[10]The Bessel functions were evaluated using computer programs written by Bradley A. Peavy of the National Bureau of Standards, and we are most grateful to him for making these available to us.

[11]E. T. Whittaker and G. N. Watson, *A Course of Modern Analysis*, 4th ed. (Cambridge U. P., London, 1927), p. 128.

[12]See Ref. 7, p. 365.