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Initial quantum-mechanical corrections to the classical transport cross sections of hard spheres

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It is shown how the known result for the viscosity cross section $Q^{(2)}$ can be extended to the unknown general cross sections $Q^{(n)}$ without repeating the complicated asymptotic analysis.

A high-energy expansion for the viscosity cross section for a Boltzmann gas of hard spheres was carried out by Boyd and Larsen,[1] who found that the expansion was nonanalytic in $\hbar$, with the first quantum correction proportional to $\hbar^{4/3}$. This contrasts with the analogous expansions for the virial coefficients of hard spheres, which include only integral powers of $\hbar$, but is similar to the result for the scattering of electromagnetic and acoustic waves by hard spheres,[2] which are series of integral powers of $(\lambda/\sigma)^{2/3}$, where λ is the wavelength and σ is the sphere diameter. The physical reason for this difference in behavior is that the quantum corrections for the cross sections are dominated by diffraction effects at the edge of the sphere,[1] whereas those for the virial coefficients are excluded-volume effects in which the spheres appear to expand in diameter by about one-fourth of the thermal deBroglie wavelength.[3]

There are other transport cross sections besides that for viscosity,[4,5] and the purpose of this Brief Report is to show how the first quantum corrections for all of these cross sections can be obtained very simply from the results of Boyd and Larsen, without having to repeat their complicated mathematical procedures.

The general transport cross sections $Q^{(n)}$ are defined as[4,5]

$$Q^{(n)}(k)=2\pi\int_0^{\pi}I(k,\theta)(1-\cos^n\theta)\sin\theta\,d\theta\ , \tag{1}$$

where $k=\mu v/\hbar$ is the wave number and $I(k,\theta)$ is the differential cross section for scattering through the angle θ. Diffusion, for example, is described by the $n=1$ cross section. By expressing $I(k,\theta)$ in terms of the phase shifts and carrying out various asymptotic expansions, Boyd and Larsen found the viscosity cross section ($n=2$) to be,

$$\frac{Q^{(2)}}{\pi\sigma^2}=\frac{2}{3}\left[1+\frac{10.376\,805}{(k\sigma)^{4/3}}+\cdots\right]. \tag{2}$$

We show how to extend this result to any value of n, by noting the behavior of $I(k,\theta)$.

Classically, the value of $I(k,\theta)$ is $\sigma^2/4$, independent of both k and θ. The dominant quantum contribution is a large forward-scattering peak, which starts at $I(k,0)=(k\sigma/4\pi)^2$ in accord with the optical theorem, and falls to approximately zero at a critical angle $\theta_c\approx\pi/k\sigma$, which is essentially determined by the uncertainty principle.[6] It is this forward peak that causes the total-scattering cross section to be $2\pi\sigma^2$ instead of the classical $\pi\sigma^2$. We can, therefore, split off the quantum correction and write

$$Q^{(n)}-Q_{\text{cl}}^{(n)}\equiv\Delta Q_{\text{qu}}^{(n)}\approx2\pi\int_0^{\theta_c}[I(k,\theta)-\tfrac{1}{4}\sigma^2](1-\cos^n\theta)\sin\theta\,d\theta\ . \tag{3}$$

This gives the leading quantum correction; there are higher-order corrections because $I(k,\theta)$ has some small oscillations at larger angles.[6] The important features here are that Eq. (3) is the leading term and that θ_c is small; other details regarding $I(k,\theta)$ are irrelevant.

Because θ_c is small, we can write

$$\cos^n\theta=(1-\tfrac{1}{2}\theta^2+\cdots)^n=1-\tfrac{1}{2}n\theta^2+\cdots\ , \tag{4}$$

whereby Eq. (3) becomes

$$\Delta Q_{\text{qu}}^{(n)}=n\pi\int_0^{\theta_c}[I(k,\theta)-\tfrac{1}{4}\sigma^2]\theta^2\sin\theta\,d\theta+\cdots\ . \tag{5}$$

The integral is the same for all values of n, so that a comparison with Eq. (2) yields the final answer,

$$\frac{\Delta Q_{\text{qu}}^{(n)}}{\pi\sigma^2}=\frac{3.458\,935\,n}{(k\sigma)^{4/3}}+\cdots\ . \tag{6}$$

Thus it is not necessary to go through another asymptotic analysis for each value of n.

This conclusion has been verified by an independent calculation of the momentum-transfer cross section ($n=1$) by Solomon and Larsen,[7] who found exactly the numerical result as given by Eq. (6). They also found, as expected, that higher-order terms did not follow this simple rule.

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