Logarithmic Density Dependence of the Transport Properties of Gases

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The authors have evaluated the coefficients of the first nonanalytic logarithmic term in the density expansion for the transport properties of a gas of hard spheres, which is due to long-range dynamical correlations between molecules. Their results resolve present uncertainties about the magnitude of the effect, appear to be consistent with available information from molecular-dynamics calculations, and satisfy bounds for the logarithmic contribution deduced from experimental viscosity data for real gases.

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In the sixties it was noticed that the transport properties of gases, i.e., the self-diffusion coefficient D, the viscosity η, and the thermal conductivity λ, cannot be represented by simple power series in terms of the density ρ. Instead, the ratios D/D_0, η/η_0, λ/λ_0, where D_0, η_0, and λ_0 are the transport coefficients in the zero-density limit as determined from the Boltzmann equation, are expected to contain a term proportional to $\rho^2 \ln\rho$. An account of the history of this discovery has been given by Brush.[1] Microscopically, the breakdown of a virial expansion for the transport coefficients finds its origin in the fact that dynamical correlations between molecules persist over distances large compared to the range of the intermolecular potential. Long-range dynamical correlations of a similar nature also lead to the presence of long-time tails in the time-correlation functions for the transport properties as first discovered from molecular-dynamics simulations.[2]

While the presence of long-range dynamical correlations is now generally accepted, there exists considerable uncertainty as to how they modify the density expansion of the transport properties. Theoretical estimates for the coefficient of the $\rho^2 \ln\rho$ term have been reported by Gervois and co-workers[3,4] and by Kan and Dorfman.[5,6] In order to determine this coefficient one needs to consider collision integrals that involve sequences of collisions among four molecules. The estimates of Gervois and co-workers are based on an explicit analysis of these four-particle collision integrals for a gas of hard spheres. Kan and Dorfman also considered a gas of hard spheres, but they replaced many of the Boltzmann operators in the collision integrals by a simplified operator from the so-called Bhatnagar-Gross-Krook model equation. The reported estimates differ by one to two orders of magnitude depending on the transport property

considered. The estimates of Gervois and co-workers seem to exceed the possible values inferred from experimental data for real gases to be discussed below, while those of Kan and Dorfman involve some serious approximations. In view of the conceptual importance of verifying the kinetic theory for the long-range dynamical molecular correlations, we decided to make an accurate analysis of the logarithmic density dependence of the transport properties for a gas of hard spheres.

According to the kinetic theory of gases, the density expansions of the transport properties can be written in the form

$$D/D_0 = 1 + D_1 \rho^* + D_2'\rho^{*2} \ln\rho^* + D_2\rho^{*2} + \ldots, \quad (1a)$$

$$\eta/\eta_0 = 1 + \eta_1 \rho^* + \eta_2'\rho^{*2} \ln\rho^* + \eta_2\rho^{*2} + \ldots, \quad (1b)$$

$$\lambda/\lambda_0 = 1 + \lambda_1 \rho^* + \lambda_2'\rho^{*2} \ln\rho^* + \lambda_2\rho^{*2} + \ldots, \quad (1c)$$

in terms of a dimensionless density $\rho^* = n\sigma^3$, where n is the number density and σ the diameter of the molecules. For a gas of hard spheres, the coefficients on the right-hand side of the expansions (1) are constants independent of temperature.

In the theory of Enskog, the density dependence of the transport properties is attributed to the excluded-volume effects that determine the virial expansion of the equilibrium properties, while successive binary collisions between the molecules are assumed to be dynamically uncorrelated. In this approximation one obtains a power series for the transport properties as a function of density with coefficients[7] $D_{1,E} = -5\pi/12 = -1.309$, $\eta_{1,E} = +7\pi/60 = +0.367$, $\lambda_{1,E} = +23\pi/60 = +1.204$, $D_{2,E}' = \eta_{2,E}' = \lambda_{2,E}' = 0$, and $D_{2,E} = +0.455$, $\eta_{2,E} = +3.795$, $\lambda_{2,E} = +3.778$. A more rigorous theoretical treatment shows that the coefficients D_1, η_1, and λ_1 of the linear terms also contain dynamical contributions from sequences of successive collisions among three molecules. The

three-particle collision integrals have been evaluated by Sengers and co-workers[8,9] and also by Brinser and Condiff.[10] Our best current estimates are[9]

$$D_1 = -1.201 \pm 0.002, \quad \eta_1 = +0.404 \pm 0.002,$$

$$\lambda_1 = +1.252 \pm 0.001. \tag{2}$$

The coefficients D_2', η_2', and λ_2' of the logarithmic contribution are determined by the asymptotic behavior of sequences of successive collisions among four particles, renormalized so as to account for a mean-free-path damping between successive collisions. A detailed analysis shows that one needs to consider ten dynamically independent four-particle collision sequences,[3] that are shown schematically in Fig. 1. As in the collision sequences associated with the three-particle collision integrals,[9] the binary collisions in the sequences can be either interacting or noninteracting. In an interacting collision the trajectories of the particles change as a result of the molecular interaction. In a noninteracting collision the particles pass through each other's in-
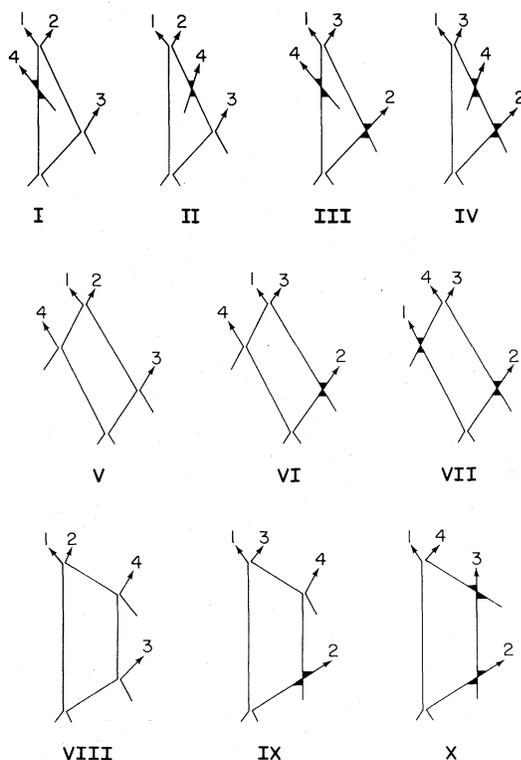

FIG. 1. Four-particle collision sequences that need to be considered in the calculation of the coefficients D_2', η_2', and λ_2'.

teraction sphere without any change of velocity; the noninteracting collisions need to be considered to correct for collisions between two molecules that are prevented from occurring by the interference of another molecule. The collision sequences labeled I through IV are dynamically the same as the three-particle collision sequences that need to be considered for the calculation of the coefficients of the linear term, except for an additional noninteracting collision with a fourth particle; the other collision sequences are genuine four-particle collision sequences.

The collision integrals are multidimensional integrals that involve the positions and velocities of four particles. Using analytical methods we reduced the collision integrals associated with sequences III and IV to two-dimensional integrals, those associated with sequences I, II, VII, and X to four-dimensional integrals, those associated with sequences VI and IX to six-dimensional integrals, and those associated with sequences V and VIII to eight-dimensional integrals. Furthermore, the contributions from sequences I and II could be incorporated into a single four-dimensional integral, thus reducing the problem to the evaluation of nine four-particle collision integrals. We have evaluated the two-dimensional integrals by numerical quadrature. The remaining collision integrals were evaluated with the same numerical Monte Carlo techniques previously employed in the evaluation of the three-particle collision integrals.[9] Our results are presented in Table I. The quoted errors represent two standard deviations. Adding up the contributions from the various collision sequences, we obtain

$$D_2' = -0.46 \pm 0.04, \quad \eta_2' = +0.30 \pm 0.03,$$

$$\lambda_2' = +0.21 \pm 0.03. \tag{3}$$

Our results are to be compared with the values $D_2' = -6.42 \pm 0.09$, $\eta_2' = +42 \pm 3$, and $\lambda_2' = +422 \pm 34$ reported by Gervois and co-workers[3,4] for a gas of hard spheres (when corrected for a numerical error[6]) and with the estimates $D_2' = -0.91$, $\eta_2' = +0.64$, and $\lambda_2' = -1.03$ found by Kan with the aid of a Bhatnagar-Gross-Krook–model approximation.[6] We conclude that the nonanalytic contributions to the density dependence of the transport properties are very much smaller than suggested by Gervois and co-workers. From Table I we see that the individual collision integrals are of order unity or slightly smaller. Since the individual contributions can either be positive or negative, the net effect is of the same order of magnitude

TABLE I. Results of theoretical calculations.

Collision sequence	D_2'	Contribution to η_2'	λ_2'
III	$+0.6864 \pm 0.0001$	-0.3939 ± 0.0001	$+0.3474 \pm 0.0001$
IV	$+0.9344 \pm 0.0001$	-0.5730 ± 0.0001	$+0.5765 \pm 0.0001$
I + II	-1.236 ± 0.008	$+0.342 \pm 0.002$	-0.188 ± 0.004
V	$+0.879 \pm 0.017$	-0.448 ± 0.013	-0.162 ± 0.010
VI	-1.297 ± 0.012	$+1.754 \pm 0.021$	-0.145 ± 0.011
VII	0	-0.600 ± 0.006	-0.057 ± 0.002
VIII	$+0.616 \pm 0.024$	-0.130 ± 0.012	$+0.112 \pm 0.013$
IX	-1.206 ± 0.019	$+0.393 \pm 0.011$	-0.685 ± 0.014
X	$+0.167 \pm 0.001$	-0.046 ± 0.001	$+0.118 \pm 0.001$
Sum	-0.456 ± 0.038	$+0.298 \pm 0.030$	$+0.206 \pm 0.025$

as the average value for the individual collision integrals. However, as a consequence of cancellations between contributions from the various collision sequences, it is difficult to predict *a priori* the sign of the logarithmic contribution for the individual transport properties. While our results generally have an order of magnitude similar to the estimates of Kan and Dorfman, we find for the thermal conductivity an effect with the opposite sign.

In order to calculate the coefficients in the density expansion for the transport properties, one customarily expands the nonequilibrium distribution function in terms of Sonine polynomials.[7,9] The results reported here correspond to the first Sonine approximation, i.e., only one Sonine polynomial was retained in the analysis. We hope to obtain estimates of higher-order Sonine approximations in the future. While they are unlikely to change the order of magnitude of the contributions from the individual collision sequences, they could affect somewhat the net results, because of the delicate balance between contributions from different collision sequences.

Information concerning the transport properties of a gas of hard spheres has been obtained from molecular-dynamics simulations. In Fig. 2 we show molecular-dynamics results at low densities obtained by Alder, Gass, and Wainwright[11] and by Erpenbeck and Wood[12] for the diffusion coefficient. Unfortunately, we cannot make a rigorous comparison between our results and the molecular-dynamics data because of the absence of a reliable theoretical estimate for the coefficient of the ρ^2 term which is closely correlated with the $\rho^2 \ln\rho$ contribution. If we approximate D_2 of the quadratic term by the value $D_{2,E}$ from the theory of Enskog, we obtain the curve shown

in Fig. 2 as a function of $\rho^* = n\sigma^3$. In this procedure we restrict ourselves to densities $\rho \lesssim 0.1$ since the theory of Enskog indicates that at densities beyond 0.1 terms of higher order than ρ^{*2} will become significant. It appears that the currently available theoretical results and the molecular-dynamics data are at least consistent with each other.

Several attempts have been made to detect a logarithmic density dependence of experimental data for the transport coefficients of gases. Among the three transport properties concerned, the viscosity is generally measured with the highest accuracy. However, even for the best experimental viscosity data one has not been able to prove the necessity of including a $\rho^2 \ln\rho$ term in the density expansion. As an alternative, Kestin and co-workers assumed the validity of the
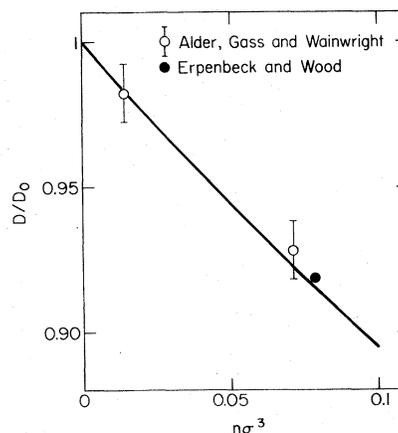

FIG. 2. The diffusion coefficient ratio D/D_0 for a gas of hard spheres as a function of $\rho^* = n\sigma^3$. The data are molecular-dynamics results and the curve is calculated from the equation $D/D_0 = 1 + D_1 \rho^* + D_2' \rho^{*2} \ln\rho^* + D_{2,E}\rho^{*2}$.

TABLE II. Summary of information from experimental viscosity data.

Gas	Temperature (°C)	σ_{eff} (Å)	η_2'
CO_2[a]	31.6	4.54	0.4 ± 0.4
Kr[b]	25.0	4.11	0.0 ± 0.6
N_2[c]	25.0	3.73	0 ± 2
Ar[c]	25.0	3.62	0 ± 2
Ne[d]	25.0	2.57	0 ± 5
Hard spheres			0.30 ± 0.03

[a]Ref. 14. [c]Ref. 13.
[b]Ref. 16. [d]Ref. 15.

theoretical form (1b) for the density expansion and tried to obtain bounds for the maximum and minimum values of the coefficient η_2' that could be consistent with the experimental viscosity data.[13-15]. The results are summarized in Table II. The values quoted for η_2' are for Eq. (1b) with $\rho^* = n\sigma_{eff}^3$, where σ_{eff} is an effective molecular diameter chosen so that the experimental dilute-gas viscosity η_0 is equal to its theoretical value for a gas of hard spheres with diameter σ_{eff}. The fits were made to experimental data at densities $\rho^* \lesssim 0.1$. A gas of hard spheres is not a good model for the first density correction to the transport coefficients, because η_1 is primarily determined by short-range correlations. However, the logarithmic term for real gases arises from the same type of long-range dynamical correlations as for a gas of hard spheres. Hence, we expect that the order of magnitude of η_2' for real gases will be roughly similar to that for a gas of hard spheres. From the information in Table II we see that our theoretical estimate η_2' $= 0.30 \pm 0.03$ for a gas of hard spheres is indeed within the range of possible values consistent with currently available experimental data. We conclude that an evaluation of the $\rho^2 \ln\rho$ term as prescribed by the kinetic theory of gases does

lead to an answer consistent with experimental evidence for real gases.

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