

# A New Dilute Gas Transport Phenomenon

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A new transport phenomenon is deduced by arguments based on the existence of nonequilibrium long-range pair correlations which persist even in a dilute gas.

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**KEY WORDS:** Dilute gas transport phenomenon; pair correlations; light scattering.

The long-range pair correlations of the preceding note<sup>(1)</sup> (equations from this note will be prefaced by a Roman numeral II) can be measured in principle by means of the random scattering of light (Rayleigh scattering) from a non-equilibrium gas. The effect is new and is in principle unobtainable from the Boltzmann equation. It is not a density correction, i.e., it persists even in the limit of extreme dilution,  $N/V \rightarrow 0$ . Unfortunately, it is numerically very small and may be impossible to measure for that reason.

Let the electric vector of the incident light wave be given by

$$\mathbf{E}_{\text{inc}}(\mathbf{r}, t) = \text{Re}[\mathbf{E}_0 \exp(i\mathbf{k}_0 \cdot \mathbf{r} - i\omega t)] \quad (1)$$

where  $\mathbf{E}_0$  is a constant vector with complex components. A typical atom, number  $j$ , at position  $\mathbf{r}_j$  produces a scattered wave of amplitude proportional to the atomic polarizability  $\alpha$ , and (in the wave zone) inversely proportional to the distance  $R$  from the effective volume to the point of observation. The effective volume is defined by the collimation of the incident light beam and by the slits of the detector of the scattered light.

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The standard theory is given by Born.<sup>(2)</sup> One must separate the total field  $\mathbf{E}$  produced by all atoms  $j$  within the effective volume into two parts: (a) an ensemble average over the statistical ensemble describing the positions of the gas particles  $\mathbf{r}_j$ ; and (b) the fluctuations about this ensemble average.

Contribution (a) leads to the complex index of refraction of the gas, while contribution (b) leads to Rayleigh scattering. This latter contribution is the only one of interest to us here. It is given by

$$\mathbf{E}_b = \operatorname{Re} \left( \frac{\alpha \mathbf{k} \times (\mathbf{E}_0 \times \mathbf{k})}{(4\pi)^{1/2} R} \sum_j \{ \exp[i(\mathbf{k}_0 - \mathbf{k}) \cdot \mathbf{r}_j] - \langle \exp[i(\mathbf{k}_0 - \mathbf{k}) \cdot \mathbf{r}_j] \rangle_{\text{av}} \} \exp(-i\omega t) \right) \quad (2)$$

where  $\mathbf{E}_0$ ,  $\mathbf{k}_0$ , and  $\omega$  are as in (1), and  $\mathbf{k}$  is the wave vector of the scattered wave, i.e.,  $|\mathbf{k}| = |\mathbf{k}_0|$  and the direction of  $\mathbf{k}$  is from the effective volume to the entry slit of the detector of scattered light. The sum over  $j$  extends over all atoms within the effective volume, and the "average" is an ensemble average over the (nonequilibrium) ensemble describing the gas.

By definition, the ensemble average of  $\mathbf{E}_b$  vanishes. But the average of  $|\mathbf{E}_b|^2$  is nonzero, and turns out to be given in terms of the one-particle distribution function  $f_1$  and the pair correlation  $\sigma(1, 2)$  [see Eq. (II.4)], by

$$\langle |\mathbf{E}_b|^2 \rangle_{\text{av}} = \frac{\alpha^2 |\mathbf{k} \times (\mathbf{E}_0 \times \mathbf{k})|^2}{4\pi R^2} \left\{ \int f_1(1) d\tau_1 + \int d\tau_1 \int d\tau_2 \sigma(1, 2) \cos[(\mathbf{k}_0 - \mathbf{k}) \cdot (\mathbf{r}_1 - \mathbf{r}_2)] \right\} \quad (3)$$

where  $d\tau = d^3\mathbf{r} d^3\mathbf{p}$  and the  $\mathbf{r}$ -integrations extend over the "effective volume" defined earlier.

The single integral is just  $N_1$ , the total number of scattering centers within the effective volume. This is the main term.

The standard result is obtained from (3) by assuming that the gas is in equilibrium. This means

$$\sigma(1, 2) = \sigma_{\text{eq}}(1, 2) = \text{const} \times \exp[-(\beta/2m)(p_1^2 + p_2^2)] \{ \exp[-\beta V(r_{12})] - 1 \} \quad (4)$$

This vanishes whenever  $r_{12} > r_0$ , the range of the interaction. As a result, the double integral in (3) is of higher order in the number density  $N/V$  than the single integral, and can therefore be ignored for a very dilute gas. The conventional formula for Rayleigh scattering then follows.

If one assumes that  $\sigma(1, 2)$  is confined to the region  $r_{12} < r_0$  even away from equilibrium, then one obtains conventional Rayleigh scattering from a

dilute gas also for nonequilibrium states. The number of atoms in the effective volume,

$$N_1 = \int f(1) d\tau_1 \tag{5}$$

may then be time dependent, but that is all.

However, the assumption regarding  $\sigma(1, 2)$  is incorrect, as pointed out in the preceding note.<sup>(1)</sup> Since  $\sigma(1, 2)$  appears explicitly in (3), and extends over distances comparable to a mean free path in nonequilibrium states, one can expect a nonzero effect even in a dilute gas.

The new effect depends upon the gas being in a nonequilibrium state. We shall illustrate it by taking the gas to be in a steady state with viscous drag. Let the gas be contained in an infinite slab between two parallel walls. Wall 1 is in the  $x$ - $y$  plane ( $z = 0$ ) and is at rest. Wall 2 is in the plane  $z = a$ , and this wall moves at constant speed  $u$  in the positive  $x$  direction. We assume that gas particles adhere to a wall before reemission into the gas. There is therefore a steady velocity gradient  $u/a$  maintained in the gas, the mean gas velocity being in the  $x$  direction with a value depending on  $z$ :

$$\langle v \rangle_{av} = (uz/a, 0, 0) \tag{6}$$

Notice that the  $x$ ,  $y$ , and  $z$  directions have been defined by this description. This will be used later.

Although the linearized Boltzmann equation is easily solved for this system, the more general equations of the preceding note<sup>(1)</sup> present rather more difficulty even for such a simple geometry. However, in the breakup of  $\sigma(1, 2)$  given by (II.5) and (II.7), the "primary" pair correlation  $\sigma_p(1, 2)$  can be obtained explicitly to a good approximation. We substitute this for  $\sigma(1, 2)$  in Eq. (3), i.e., we neglect the Rayleigh scattering produced by  $\sigma_m(1, 2)$ . This should give a lower bound for the true Rayleigh scattering, since  $\sigma_m(1, 2)$  is "driven by"  $\sigma_p(1, 2)$  in the equations, and is a correlation in the same general direction, only less pronounced.

The resulting calculation is rather lengthy, with very awkward integrals. The final result is best stated in terms of the ratio

$$R = \frac{\text{intensity of scattered light from nonequilibrium state}}{\text{intensity of scattered light from gas in equilibrium}} \tag{7}$$

We define

$$\boldsymbol{\kappa} = \mathbf{k}_0 - \mathbf{k} \tag{8}$$

and we let  $\kappa$  be the magnitude of this vector, and  $\theta_\kappa$  and  $\phi_\kappa$  be its polar angles with respect to the  $x$ ,  $y$ ,  $z$  directions defined earlier. We then get the result (for a hard-sphere gas)

$$R = 1 - \frac{15}{32} \left( \frac{\pi m}{k_B T} \right)^{1/2} \frac{u}{\kappa a} (\cos \theta_\kappa \sin \theta_\kappa \cos \phi_\kappa) G(\kappa \Lambda) \tag{9}$$

where  $m$  is the atomic mass,  $k_B$  the Boltzmann constant,  $T$  the temperature, and  $\Lambda$  the mean free path. The function  $G$  is complicated but has the property

$$G(\kappa\Lambda) = 1 \quad \text{for } \kappa\Lambda \gg 1 \quad (10)$$

$$G(\kappa\Lambda) = \text{const} \times (\kappa\Lambda)^3 \quad \text{for } \kappa\Lambda \ll 1 \quad (11)$$

The "constant" is the numerical value of a complicated integral, of order unity. The condition  $\kappa\Lambda \gg 1$  means that the mean free path  $\Lambda$  is much bigger than the wavelength of the light.

The angular dependence in (9) is on the angles  $\theta_\kappa, \phi_\kappa$  of the vector (8), and is therefore very characteristic for this phenomenon. The effect is proportional to the velocity gradient  $u/a$  and goes to zero in equilibrium. The expression (9) is independent of the density  $N/V$ , i.e., the effect is *not* a density correction. In the limit  $\kappa\Lambda \gg 1$  it does not even depend on the value of the mean free path  $\Lambda$ . The effect occurs in the extreme dilute gas regime but cannot be deduced from the Boltzmann equation: That equation does not contain  $\sigma(1, 2)$ , which is the essential quantity for the new effect. One can use the conventional derivation of the Boltzmann equation to obtain information about the pair correlation immediately following a binary collision, i.e., about our  $\sigma_p(1, 2)$  at  $r_{12} = r_0$  ( $r_0$  is the range of the interaction). However, one needs to know the decay law for the correlation as a function of  $r_{12}$  to obtain the result (11); and, in principle, one also requires the nonsingular contribution  $\sigma_m(1, 2)$  for a complete calculation. Since neither of these can be obtained from the standard arguments about the Boltzmann equation, we conclude that the new effect is beyond the reach of that theory. We note in particular that the theory of Ref. 4 does not give our results; rather, it would lead to Eq. (10) for *all* values of the mean free path and of the wavelength of light.

Unfortunately, the magnitude of the new effect appears to be extremely small for experimental detection. Hence this effect may be more a matter of principle for theorists than a prediction of a feasible experimental measurement. The theoretical point, however, seems to have some significance.

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