

Long-Range Pair Correlations in Dilute Gases

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It is shown that there exist nonequilibrium pair correlations which are not described by the Boltzmann transport equation but which persist even in a dilute gas.

KEY WORDS: Boltzmann transport equation; dilute gases; nonequilibrium pair correlations.

The Boltzmann equation, which is used to describe the nonequilibrium behavior of dilute gases, is generally believed to become exact for very dilute gases. There are three possible meanings of this assertion:

(A) All physically measurable effects in a dilute gas are described correctly by the Boltzmann equation; in particular, the pair correlations (which are ignored) really do become vanishingly small.

(B) The Boltzmann equation for the one-particle reduced distribution function describes correctly all physical measurements of sums of one-particle quantities in a dilute gas, but possibly not other measurements.

(C) The Boltzmann equation becomes exact in the extreme "Boltzmann-Grad limit,"⁽¹⁾ that is

$$N/V \rightarrow \infty, \quad Nr_0^3/V \rightarrow 0, \quad Nr_0^2/V = \text{finite constant}$$

where r_0 is the range of the force between two particles.

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In this note we point out that (A) is certainly incorrect; we make no statement about (B) or (C), but note that our effects approach zero in the Boltzmann–Grad limit.

Referring to the preceding paper (Ref. 3; equations from that paper are preceded by a Roman numeral I) we obtain the dilute gas limit of equations (I.4) and (I.5) by integrating the Poisson bracket terms over the interaction region [where $V_{12} = V(r_{12})$ is nonzero] and then letting the range of the interaction become small.

This limit turns out to be somewhat intricate, for the following reason: Immediately after a (1, 2) collision, the two particles separate along the paths

$$\mathbf{r}_i(t) = \mathbf{r}_i(t_c) + (\mathbf{p}_i/m)(t - t_c), \quad i = 1, 2 \quad (1)$$

where t_c is the collision instant, and \mathbf{p}_i is the momentum of particle i after the collision. In the low density limit, we may ignore molecular-size effects, so that

$$\mathbf{r}_1(t_c) = \mathbf{r}_2(t_c) \quad (2)$$

i.e., the two particles start at $t = t_c$ from the same point. One then obtains from (1) by subtraction

$$\mathbf{r}_2(t) - \mathbf{r}_1(t) = [(t - t_c)/m][\mathbf{p}_2(t) - \mathbf{p}_1(t)] \quad (3)$$

Relation (3) continues to hold until one of the particles collides with a third particle, i.e., it persists on average during times of the order of a mean free time between collisions.

Relation (3) has extremely strong consequences for the properties of $\sigma(1, 2)$ in

$$f_2(1, 2) = f_1(1)f_1(2) + \sigma(1, 2) \quad (4)$$

The function $\sigma(1, 2) = \sigma(\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2; t)$ must be written as a sum of two parts

$$\sigma(1, 2) = \sigma_p(1, 2) + \sigma_m(1, 2) \quad (5)$$

where $\sigma_p(1, 2)$ describes the “primary” pair correlation, which obeys (3), and $\sigma_m(1, 2)$ is the residual pair correlation remaining after multiple collisions. There is no need to separate $\sigma_m(1, 2)$ into terms classified by the precise number of collisions suffered by 1 and/or 2 between t_c and t ; $\sigma_m(1, 2)$ describes the sum of all these terms at time t . The pair correlation $\sigma_p(1, 2)$ would also be found in an exact theory which retains correlations of all orders. On the other hand, $\sigma_m(1, 2)$ would appear in such a theory as an integral over triplet and higher correlations, not as a direct pair correlation at all.

The function $\sigma_m(\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2, t)$ is a smooth function of all its variables; but σ_p is far from smooth. Rather,

$$\sigma_p(\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2, t) = 0 \quad \text{unless } \mathbf{r}_2 - \mathbf{r}_1 \text{ is parallel to } \mathbf{p}_2 - \mathbf{p}_1 \quad (6)$$

This follows from (3) since $(t - t_c)/m$ is a positive scalar multiplier. Unless the integral of σ_p vanishes altogether, (6) implies a twofold delta-function behavior for σ_p ; we introduce $\mathbf{R} = \frac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2)$, $\mathbf{P} = \mathbf{p}_1 + \mathbf{p}_2$, $\mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1$, $\mathbf{p} = \frac{1}{2}(\mathbf{p}_2 - \mathbf{p}_1)$, and we let the polar angles of \mathbf{r} be θ_r, ϕ_r , those of \mathbf{p} be θ_p, ϕ_p . Then σ_p in the dilute gas limit has the form

$$\sigma_p(\mathbf{R}, \mathbf{P}, r, \theta_r, \phi_r, p, \theta_p, \phi_p, t) = \omega(\mathbf{R}, \mathbf{P}, r, \theta_r, \phi_r, p, t)(1/r^2) \delta(\cos \theta_r - \cos \theta_p) \delta(\phi_r - \phi_p) \quad (7)$$

where ω is defined by (7) and is a function of the indicated variables.

In order to go to the low-density limit of equations (I.4) and (I.5), it is essential to introduce (5) and (7) for $\sigma(1, 2)$. One then obtains coupled integrodifferential equations for the three functions $f_1(\mathbf{r}_1, \mathbf{p}_1, t)$; $\omega(\mathbf{R}, \mathbf{P}, r, \theta_r, \phi_r, p, t)$, and $\sigma_m(\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2, t)$. The equations are rather lengthy, and we shall confine ourselves here to enumerating some of their consequences.

(1) In the equilibrium state of the gas, $\omega = \sigma_m = 0$. The equilibrium pair correlations (which do exist) are confined to the interaction region, $r_{12} < r_0$, which region is being ignored here. In the integrodifferential equations, the way this happens is that the source term for $\partial\omega/\partial t$ cancels to zero if f_1 has the equilibrium form. The cancellation in question is the same which, in the Boltzmann equation, leads to stability of the Maxwell-Boltzmann distribution against collisions.

(2) Away from equilibrium, in general, neither ω nor σ_m vanishes. That is, *there exist nonequilibrium pair correlations, not included in the Boltzmann equation.*

(3) These nonequilibrium pair correlations include extremely strong, delta-function-like, correlations between the position and momentum vectors of the two particles; see Eq. (7). *As a consequence, it is neither exactly true, nor even a good first approximation, to assume that the momentum dependence is that of a Maxwell distribution.* The Maxwell distribution for the two particle projection $f_2(1, 2)$ gives the momentum dependence

$$\exp[-(\beta/2m)(p_1^2 + p_2^2)] = \exp[-(\beta P^2/4m) - (\beta p^2/m)] \quad (8)$$

This does not allow for any directional correlation between the vectors $\mathbf{p} = \frac{1}{2}(\mathbf{p}_2 - \mathbf{p}_1)$ and $\mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1$, and is therefore quite insufficient if terms of type σ_p [Eq. (7)] are dominant—as they are. This is, in our opinion, a major cause of the inadequacies of the Ansatz (I.8) of Enskog,⁽⁴⁾ of the Rice-Allnatt theory,⁽⁵⁾ and of the many other attempts to obtain generalizations of the Boltzmann equation. All these approaches assume that correlations between positions and momenta vanish.

(4) The nonequilibrium pair correlations have a range, in the variable $r = |\mathbf{r}_2 - \mathbf{r}_1|$, of the order of the mean path Λ . Beyond this, they go to zero in an exponential fashion. The effect of this is that the integral

$$\int d^3r \int d^3p \sigma(\mathbf{R}, \mathbf{P}, \mathbf{r}, \mathbf{p}, t)$$

converges as it stands. There is no divergence associated with an infinite region of integration, since the integrand vanishes exponentially for large r . It is likely, therefore, that similar integrals, which arise in the theory of the density dependence of transport coefficients, will also be convergent automatically, thereby solving a divergence difficulty of the usual theories pointed out by Cohen,⁽⁶⁾ without any need to re-sum a series of diagrams.

(5) The existence of a long-range, singular pair correlation away from equilibrium is also implicit in the work of Kritz *et al.*⁽⁷⁾ and Pomeau.⁽⁸⁾ However, their theory fails to give the exponential decay with increasing r_{12} , and therefore not only disagrees with our results, but also violates the finite-range property described in the preceding paragraph.

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