

# Kinetic description of hydrodynamic motion: Entropy balance and hydrodynamic fluctuations with self-diffusion

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A kinetic equation which incorporates small-scale and large-scale fluctuations simultaneously is proposed for use in deriving hydrodynamic equations for arbitrary Reynolds numbers. A perturbation theory is constructed in the reciprocal of the number of particles in a physically infinitesimal volume. An entropy balance equation and fluctuation spectra are derived; self-diffusion is taken into account.

A statistical derivation of the hydrodynamic equations for gases is based on an approximate solution of the Boltzmann equation.<sup>1,2</sup> Serving as small parameter is the product of the Knudsen and Mach numbers:  $KM \ll 1$ . The zeroth approximation corresponds to a local Maxwellian distribution. The functions  $\rho$ ,  $u$ , and  $T$  which appear in this distribution satisfy the hydrodynamic equations without dissipative terms. Dissipative terms arise only in the next approximation. Just how small these terms are is characterized by the reciprocal of the Reynolds number:  $1/Re = K/M \ll 1$ . These two conditions are compatible only at  $M \sim 1$ .

At small Reynolds numbers, a perturbation theory in the solution of the kinetic equation is not an adequate basis for deriving hydrodynamic equations.

For liquids, the mean free path  $l$  is on the order of the average distance between atoms,  $r_{av}$ , so a local distribution replacing a local Maxwellian distribution can now be derived only from the condition for a maximum of the local entropy, under appropriate nonequilibrium auxiliary conditions.<sup>3</sup> Here again, the transition to hydrodynamic equations is usually based on a perturbation theory in the Knudsen number, so the region of small Reynolds numbers again drops out of the picture.

To derive hydrodynamic equations for arbitrary Reynolds numbers in the present letter, we use a kinetic equation which incorporates small-scale and large-scale fluctuations simultaneously. The dissipation is therefore described by two corresponding "collision integrals":

$$\frac{\partial f}{\partial t} + \mathbf{v} \frac{\partial f}{\partial \mathbf{R}} + \frac{\mathbf{F}}{m} \frac{\partial f}{\partial \mathbf{v}} = I(\mathbf{R}, \mathbf{v}, t) + \frac{\partial}{\partial \mathbf{R}} \left[ D \frac{\partial f}{\partial \mathbf{R}} - \frac{D}{kT} \mathbf{F} f \right]; \quad \frac{D}{kT} = b, \quad (1)$$

where  $b$  is the mobility of the atoms. The boundary between the regions of small-scale and large-scale fluctuations is represented by physically infinitesimal length scales in a hydrodynamic description (see Ch. 7 in Ref. 2). In determining these length scales, we can distinguish between two cases. 1. *Slow processes.* The scale values  $\tau_{ph}$  and  $l_{ph}$  are

related by a diffusion law,  $\tau_{ph} \sim l_{ph}^2/D$ . Here  $D$  is one of three kinetic coefficients in hydrodynamics: the self-diffusion coefficient  $D$ , the kinematic viscosity  $\nu$ , or the thermal diffusivity  $\chi$ . Equation (1) is written for the very simple case  $D = \nu = \chi$ . Distinctions among  $D$ ,  $\nu$ , and  $\chi$  are introduced in the hydrodynamic equations. 2. *Fast (acoustic) processes*. In this case we use the relation  $D = \nu = \chi$ . In accordance with these two cases, the switch to the hydrodynamic equations is based on the existence of two small parameters:

$$K_{ph} = \frac{l_{ph}}{L} \sim \frac{1}{\sqrt{N_{ph}}} \sim K^{3/5}; \quad K_{ph} = \frac{l_{ph}}{L} \sim K^{1/2}, \quad N_{ph} = \frac{\tau_D}{\tau_{ph}} \gg 1. \quad (2)$$

The small parameters are thus determined by powers of the Knudsen number or powers of the parameter  $N_{ph}$ , which is the average number of particles in a physically infinitesimal volume. In the last expression in (2),  $\tau_D$  is the diffusion relaxation time, and  $\tau_{ph}$  is a physically infinitesimal time interval.

In the zeroth approximation in  $1/\sqrt{N_{ph}}$  we find from (1) the equation  $I(\mathbf{R}, \mathbf{v}, t) = 0$ . That equation determines a locally equilibrium distribution  $f_0(\mathbf{R}, \mathbf{v}, t)$ , which depends on the hydrodynamic functions  $\rho$ ,  $\mathbf{u}$ ,  $T$ . To determine them, we substitute the distribution  $f_0$  into Eq. (1) and make the transition to the hydrodynamic equations. The mass flux in the continuity equation is determined by the sum of three components: convective transport  $\rho \mathbf{u}$ , self-diffusion, and the external force  $\mathbf{F}$ . In the equilibrium state, Eq. (1) for the function  $f_0$  is satisfied by a Maxwell-Boltzmann distribution and by the Einstein relation  $D = bkT$ . Finally, we note that the appearance of the second dissipative term in (1) reflects slow processes with a minimum time  $(\tau_D)_{\min}$  on the order of  $\tau_{ph}$ .

A different approach was taken in Refs. 4 and 5 to deal with large-scale fluctuations in hydrodynamics. In particular, fluctuation-related increments in the sound velocity and in the attenuation coefficient were found. These corrections are on the order of  $\sqrt{K}$ , in agreement with estimates (2). On the whole, however, the approach of the present letter is not equivalent to that developed in Refs. 4 and 5.

When self-diffusion is taken into account, but with  $F = 0$ , the entropy flux and the entropy production are described by the expressions

$$j_s(\mathbf{R}, t) = (\rho \mathbf{u} - D \text{grad } \rho) s + \frac{k}{m} D \text{grad } \rho - \frac{C_V \rho}{T} \chi \text{grad } T, \quad (3)$$

$$\sigma(\mathbf{R}, t) = \frac{k}{m} \left[ D \rho \left( \frac{\text{grad } \rho}{\rho} \right)^2 + \nu \rho \frac{m}{kT} \left( \frac{\partial u_i}{\partial R_i} \right)^2 + C_V \rho \chi \left( \frac{\text{grad } T}{T} \right)^2 \right].$$

According to the second law of thermodynamics, we would have  $\sigma \geq 0$ .

We turn now to the results calculated for equilibrium fluctuations. For the low-frequency region, the spectra of the density, the temperature, and the entropy are described by

$$(\delta\rho\delta\rho)_{\omega, \mathbf{k}} = \frac{2D\mathbf{k}^2}{\omega^2 + (D\mathbf{k}^2)^2} \frac{k\rho}{C_p}; \quad (\delta T\delta T)_{\omega, \mathbf{k}} = \frac{2\chi\mathbf{k}^2}{\omega^2 + (\chi\mathbf{k}^2)^2} \frac{kT^2}{\rho C_p}; \quad (4)$$

$$(\delta s\delta s)_{\omega, \mathbf{k}} = \left[ \left(1 - \frac{C_V}{C_p}\right) \frac{2D\mathbf{k}^2}{\omega^2 + (D\mathbf{k}^2)^2} + \frac{C_V}{C_p} \frac{2\chi\mathbf{k}^2}{\omega^2 + (\chi\mathbf{k}^2)^2} \right] C_p \frac{k}{\rho}. \quad (5)$$

The width of the fluctuation spectrum is thus determined completely by the self-diffusion coefficient, and that of the temperature spectrum by the thermal diffusivity. Accordingly, the spectrum of entropy fluctuations is the sum of two lines, whose relative contributions depend on the ratio  $C_V/C_p$ . In this manner, the condition of a complete correlation of the fluctuations  $\delta\rho$  and  $\delta T$  is lifted for all frequencies. A complete correlation holds only for fluctuation characteristics of an integral nature in  $\omega$ .

The width of the spectra of the fluctuations in the density, the temperature, the pressure, and the velocity in the high-frequency region is determined by a combination of the three dissipative coefficients  $D$ ,  $\chi$ , and  $\nu$ :

$$\gamma = \frac{1}{2} \left[ \nu + \frac{C_V}{C_p} D + \left(1 - \frac{C_V}{C_p}\right) \chi \right] \mathbf{k}^2. \quad (6)$$

We see that the answer to the old question of whether self-diffusion should or should not be incorporated in the hydrodynamic equations can be found by analyzing the spectra of molecular scattering of light in liquids with different values of the kinetic coefficients  $D$  and  $\chi$ . We also note that the presence of a Boltzmann distribution is actually proof that there is a mass transfer by virtue of self-diffusion in an inhomogeneous medium. From the standpoint of the theory of irreversible processes, this distribution is established as the result of a balance between the mass flux set up by the external field and the mass flux caused by self-diffusion. The balance between these processes is determined by the second expression on the right side of Eq. (1).

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<sup>2</sup>Yu. L. Klimontovich, *Statistical Physics*, Nauka, Moscow, 1982.

<sup>3</sup>D. N. Zubarev, *Nonequilibrium Statistical Thermodynamics*, Nauka, Moscow, 1971.

<sup>4</sup>A. F. Andreev, *Zh. Eksp. Teor. Fiz.* **75**, 1511 (1978) [*Sov. Phys. JETP* **48**, 763 (1978)].

<sup>5</sup>V. G. Morozov, *Physica A* **117**, 511 (1983).

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