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CONTRIBUTION TO THE THEORY OF THE BULK VISCOSITY COEFFICIENT

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It is shown that the bulk viscosity coefficient of an adiabatically isolated system is defined by a complex function of the frequency. Some properties of the function are investigated. Pressure fluctuations in such a system are also considered.

THE general statistical theory developed by Kubo [1] for linear dissipative processes in systems consisting of a large number of particles yields rigorously-derived expressions for the admittances only when dealing with the reaction of the system to external forces of dynamic origin, which can be included in the Hamiltonian. The case of "thermal" external forces does not admit of a fully rigorous or sufficiently detailed analysis[2]. It has been shown by Montroll[3], however, with special application to the problem of shear viscosity, that a definite canonical transformation of the coordinates and momenta of the system particles makes it possible to separate in the Hamiltonian the term describing the shear deformation, and then calculate the coefficient of shear viscosity.

We show in this paper that by means of a suitable canonical transformation we can separate in the Hamiltonian the term describing the isotropic compression or dilatation, and calculate the coefficient of bulk viscosity for an adiabatically isolated system. In accordance with the general fluctuation-dissipation theorem[4], the coefficient of bulk viscosity is connected with the correlation function of the pressure fluctuations. This makes it possible to obtain by non-thermodynamic means an expression for the fluctuations of the pressure in an adiabatically isolated system.

The equation which determines the coefficient of bulk viscosity relates the change in the trace of the stress tensor $\sigma_{\mu\nu}$ (μ, ν = 1, 2, 3) with changes in the system density. For adiabatic processes under infinitesimally small changes in the density ρ and velocity **v** in the system, the trace of the stress tensor can be written in the form (see, for example, [5]):

$$ {}^1/_3\sigma_{\mu\mu} = -p_0 - (\partial p / \partial\rho)_{0,S}\rho' + \zeta \operatorname{div} \mathbf{v}. \tag{1}$$

It is assumed here that $\rho = \rho_0 = \rho'$ and $p = p_0 + (\partial p/\partial\rho)_{0,S}\rho'$, and that ρ' and **v** are infinitesimally small; ρ_0 and p_0 are the equilibrium density and hydrostatic pressure; ζ in formula (1) is the coefficient of bulk viscosity. For periodic time variations of ρ' and **v** we can rewrite (1), using the linearized continuity equation, in the form

$$\begin{aligned} {}^1/_3\sigma_{\mu\mu} &= -p_0 + \mathbf{Re}\{(i\omega^{-1}[\rho(\partial p / \partial\rho)_S]_0 + \zeta) \operatorname{div} \mathbf{v}\} \\ &= -p_0 + \operatorname{Re}\{Z_S(\omega) \operatorname{div} \mathbf{v}\}, \qquad \mathbf{v} = \mathbf{v}_0 e^{-i\omega t}. \end{aligned} \tag{2}$$

It will be shown below that the bulk viscosity and the elasticity can be naturally combined into a single complex coefficient of bulk viscosity $Z_S(\omega)$. In the limiting case of low frequencies, when the usual hydrodynamic equations are valid, it follows from (2) that

$$\begin{gathered} \lim_{\omega\to 0} \zeta(\omega) \equiv \lim_{\omega\to 0} \operatorname{Re}\{Z_S(\omega)\} = \zeta, \\ \lim_{\omega\to 0} K_S(\omega) \equiv \lim_{\omega\to 0} \omega \operatorname{Im}\{Z_S(\omega)\} = [\rho(\partial p/\partial\rho)_S]_0. \end{gathered} \tag{3}$$

With the aid of (2) we can calculate the quantity $\sigma_{\mu\mu}V/3$ in a state that differs little from equilibrium

$$\begin{aligned} {}^1/_3\sigma_{\mu\mu}V &= -p_0V_0 + \operatorname{Re}\{V_0(-i\omega^{-1}[V(\partial p / \partial V)_S]_0 \\ &\quad - i\omega^{-1}p_0 + \zeta) \operatorname{div} \mathbf{v}\} \\ &= -p_0V_0 + \operatorname{Re}\{V_0 Z_1(\omega) \operatorname{div} \mathbf{v}\}, \end{aligned} \tag{4}$$

where V_0—equilibrium volume of the system, $V = V_0 + V'$, and V' is infinitesimally small. The reason for considering the quantity $\sigma_{\mu\mu}V/3$ will be made clear later. From (2) and (4) we get the following connection between the functions $Z_S(\omega)$ and $Z_1(\omega)$:

$$Z_S(\omega) = Z_1(\omega) + ip_0 / \omega. \tag{5}$$

2. We shall now show how the Kubo formalism [1] can be used to calculate the function $Z_S(\omega)$, which relates the change in the stress-tensor trace with the changes in density. Let the system (we are considering a classical system, since quantum effects can be neglected for the majority of liquids at temperatures far from absolute zero;

in addition, the quantum generalization presents no special difficulties[1]), consist of N identical molecules and let it be contained in a vessel in the form of a cube with edge L ($L^3 = V_0$). The coordinates and momenta of the centers of mass of the molecules are respectively $\mathbf{R}_j$ and $\mathbf{P}_j$ ($j = 1, 2, \ldots, N$), and $\{\xi_j\}$ is the aggregate of coordinates and momenta corresponding to the rotational and intramolecular (vibrational) motions of the j-th molecule. We write the Hamiltonian of the system in the form

$$H = H_c + \overline{H},$$

$$H_c = \sum_{j=1}^{N} \frac{\mathbf{P}_j^2}{2m} + \frac{1}{2} \sum_{i \neq j=1}^{N} U(\mathbf{R}_{ij}, \{\xi_i\}, \{\xi_j\}),$$

$$\overline{H} = \overline{H}(\{\xi_1\}, \ldots, \{\xi_N\}), \tag{6}$$

i.e., H_c is the part of the Hamiltonian describing the motions of the molecule mass centers, and $\overline{H}$ is part of the Hamiltonian corresponding to the rotational and vibrational motions. In (6), m is the mass of the molecule, $U(\mathbf{R}_{ij}, \{\xi_i\}, \{\xi_j\})$ is the potential energy of interaction of molecule pairs, which can depend on the rotational and vibrational states of the interacting molecules, and $\mathbf{R}_{ij} = \mathbf{R}_i - \mathbf{R}_j$.

We introduce new coordinates and momenta with the aid of the relations

$$\mathbf{r}_j = \mathbf{R}_j e^a, \quad \mathbf{p}_j = \mathbf{P}_j e^{-a}, \quad \{\xi_j'\} = \{\xi_j\}, \tag{7}$$

where a does not depend on the coordinates or momenta, but can be a function of the time t. It is easy to see that the transformation (7) is canonical. The change in the vessel dimensions under this transformation can be described by the formula

$$l = e^a L, \qquad V = V_0 e^{3a}. \tag{8}$$

In the new variables, for infinitesimally small a, the Hamiltonian takes the form

$$H(a) = H(0) + a\Big\{ \sum_{j=1}^{N} \frac{\mathbf{p}_j^2}{m} - \frac{1}{2} \sum_{i \neq j=1}^{N} \mathbf{r}_{ij} \frac{\partial}{\partial \mathbf{r}_{ij}} U(\mathbf{r}_{ij}, \{\xi_i\}, \{\xi_j\}) \Big\}, \tag{9}$$

where H(0)—unperturbed Hamiltonian coinciding with (6).

If we assume that a depends on the time, $a = F(t)$, then the expression (9) takes the form

$$H(a) = H(0) - AF(t), \tag{10}$$

where

$$A = -\sum_{j=1}^{N} \frac{\mathbf{p}_j^2}{m} + \frac{1}{2} \sum_{i \neq j=1}^{N} \mathbf{r}_{ij} \frac{\partial U(\mathbf{r}_{ij}, \{\xi_i\}, \{\xi_j\})}{\partial \mathbf{r}_{ij}}. \tag{11}$$

It can be easily seen from (8) that a is proportional to the relative change in the vessel volume (for an infinitesimally small change in volume): $a = V'/3V_0$. On the other hand, the quantity A averaged over the equilibrium Gibbs ensemble (the averaging here and throughout is both over the coordinates and momenta of the mass centers, and over the rotational and vibrational states of the molecules), is proportional to the trace of the stress tensor of the system:

$$\langle A \rangle = (\sigma_{\mu\mu} V)_0 = -3 p_0 V_0. \tag{12}$$

In the absence of rotations and vibrations, the dynamical quantity A coincides with the analogous quantity obtained by others from different considerations (see, for example, [6]), while formula (12) under these conditions is a long known result [7,8]. Thus, the term $-AF(t)$ in (10) describes the work of isotropic compression or dilatation of the system.

If the dimensions of the vessel vary in accordance with (8), we obtain in the coordinate system defined by the first relation in (7) the following expression for the velocity field:

$$\mathbf{v} = \mathbf{r}\dot{F}(t), \qquad \operatorname{div} \mathbf{v} = 3\dot{F}(t) \tag{13}$$

(the dot denotes differentiation with respect to time). Assuming that the driving force F(t) has a periodic time dependence

$$F(t) = F_0 e^{\varepsilon t} \cos \omega t, \qquad F(-\infty) = 0 \tag{14}$$

(ϵ—small positive constant that ensures adiabatic turning on of the perturbation $-AF(t)$ in the remote past; in the final results it should be set equal to zero), and substituting (13) in (14), we obtain

$${}^1/_3 \sigma_{\mu\mu} V + p_0 V_0 = -3 \operatorname{Re}\{V_0 Z_1(\omega) i\omega e^{\varepsilon t - i\omega t} F_0\}, \tag{15}$$

and then, using the condition $F(-\infty) = 0$, we get

$$\int_{-\infty}^{t} ({}^1/_3 \sigma_{\mu\mu}(t) V(t) + p_0 V_0)\, dt = 3 \operatorname{Re}\{V_0 Z_1(\omega) e^{\varepsilon t - i\omega t} F_0\}. \tag{16}$$

Expression (16) shows that to calculate $Z_1(\omega)$ we must consider the variation of the quantity

$$B = \frac{1}{3} \int_{-\infty}^{t} (A(t) - \langle A \rangle)\, dt \tag{17}$$

(the quantities A and $\langle A \rangle$ are defined by (11) and (12) respectively; the function A(t) describes the time evolution of the function $A(\mathbf{p}_1, \ldots, \mathbf{p}_N, \mathbf{r}_1, \ldots, \mathbf{r}_N, \{\xi_1\}, \ldots, \{\xi_N\})$ in the course of natural motion), due to the presence of the perturbation $-AF(t)$ which describes the change in the volume of the system. Using the Kubo formalism[1], we get

$$\langle \Delta B\rangle = 3\,\mathrm{Re}\{V_0 Z_1(\omega)\, e^{-i\omega t} F_0\}, \tag{18}$$

$$Z_1(\omega) = \frac{1}{9kTV_0}\lim_{\varepsilon\to 0}\int_0^\infty e^{i\omega t-\varepsilon t}\langle (A(t)-\langle A\rangle)A(0)\rangle\, dt \tag{19}$$

(k—Boltzmann constant, T—absolute temperature; the averaging ⟨...⟩ is over an equilibrium Gibbs ensemble referred to the instant $t = 0$).

Substituting (19) in (5), we get an expression for the complex coefficient of bulk viscosity $Z_S(\omega)$:

$$Z_S(\omega) = \frac{i}{\omega}p + \frac{1}{9kTV}\lim_{\varepsilon\to 0}\int_0^\infty e^{i\omega t-\varepsilon t}\langle (A(t)-\langle A\rangle)A(0)\rangle\, dt \tag{20}$$

(the zero subscript for the pressure and volume has been left out for simplicity). This formula leads to expressions for the frequency-dependent coefficient of bulk viscosity and isotropic-compression modulus

$$\zeta(\omega) = \mathrm{Re}\,\{Z_S(\omega)\} = \frac{1}{9kTV}\mathrm{Re}\left\{\lim\int_0^\infty e^{i\omega t-\varepsilon t}\langle (A(t)-\langle A\rangle)A(0)\rangle\, dt\right\},$$

$$K_S(\omega) = \omega\,\mathrm{Im}\,\{Z_S(\omega)\} = p + \frac{1}{9kTV} \times \mathrm{Im}\left\{\omega\lim_{\varepsilon\to 0}\int_0^\infty e^{i\omega t-\varepsilon t}\langle (A(t)-\langle A\rangle)A(0)\rangle\, dt\right\}. \tag{21}$$

3. Let us investigate our result. At low frequencies expressions (21) become

$$\zeta(0) = \frac{1}{9kTV}\int_0^\infty \langle A(t)A(0) - A^0A^0\rangle\, dt,$$

$$K_S(0) = p + \frac{1}{9kTV}(\langle A^0A^0\rangle - \langle A\rangle^2), \tag{22}$$

where A^0 denotes the invariant part of A, i.e., the part which does not change in time when the system is in natural motion. The term $\langle A^0A^0\rangle$ is obtained by going to the limit (see [1]):

$$\langle A^0A^0\rangle = \lim_{t\to\infty}\langle A(t)A(0)\rangle. \tag{23}$$

Formulas (22) must be compared with (3), which is usually used in hydrodynamics, and which describes correctly processes that vary slowly in time; as a result we get

$$\zeta = \frac{1}{9kTV}\int_0^\infty \langle A(t)A(0) - A^0A^0\rangle\, dt,$$

$$-V\left(\frac{\partial p}{\partial V}\right)_S = p + \frac{1}{9kTV}(\langle A^0A^0\rangle - \langle A\rangle^2). \tag{24}$$

At high frequencies (but not higher than a certain maximum frequency, above which the concept of collective motions becomes meaningless) expressions (21) tend to the following limits:

$$\lim_{\omega\to\infty}\zeta(\omega) = 0,\quad K_S(\infty) = p + \frac{1}{9kTV}(\langle A^2\rangle - \langle A\rangle^2). \tag{25}$$

Owing to the symmetry of the function $\langle A(t)A(0)\rangle$ relative to time reversal, the quantity $\zeta(\omega)$ tends to zero more rapidly than any power of $1/\omega$. Thus, the shear-viscosity coefficient decreases rapidly with increasing frequency, and the quantity $K_S(\omega)$ changes from one finite value $K_S(0)$ to a generally speaking different value $K_S(\infty)$:

$$K_S(\infty) - K_S(0) = \frac{1}{9kTV}(\langle A^2\rangle - \langle A^0A^0\rangle). \tag{26}$$

The difference between $K_S(\infty)$ and $K_S(0)$ vanishes only in the case of an ideal monatomic gas, for then A^0 coincides with A (for an ideal gas, as can be seen from (11), A is proportional to the total energy, which is an integral of the motion). It follows from the first formula of (22) that $\zeta(0) = \zeta = 0$, i.e., the bulk viscosity of an ideal monatomic gas is equal to zero.

We note that the theory developed here leads to the relaxation theory of Mandel'shtam and Leontovich[9] if we put for the correlation function in (20)

$$\langle A(t) - \langle A\rangle)A(0)\rangle = \langle A^0A^0\rangle - \langle A\rangle^2 + (\langle A^2\rangle - \langle A^0A^0\rangle)e^{-t/\tau}, \tag{27}$$

where τ is some relaxation time.

4. As already mentioned, the complex coefficient of bulk viscosity $Z_S(\omega)$ is connected with the Fourier transform of the correlation function of the pressure fluctuations in the system. In fact, as noted above, the dynamical quantity A is, apart from coefficients, the microscopic expression for the pressure (at constant volume). Therefore the function $\langle (A(t) - \langle A\rangle)A(0)\rangle$ is proportional to the correlation function of the pressure fluctuations, and the quantity $(\langle A^2\rangle - \langle A\rangle^2)$ is proportional to the mean value of the pressure fluctuations, i.e.,

$$\overline{(\Delta p)^2} = (\langle A^2\rangle - \langle A\rangle^2)\,/\,9V^2. \tag{28}$$

It then follows from (25) that

$$\overline{(\Delta p)^2} = (K_S(\infty) - p)kT\,/\,V, \tag{29}$$

i.e., the mean value of the pressure fluctuations in an adiabatically isolated system is expressed in terms of the modulus of isotropic compression at high frequencies. It must be emphasized that this exact result was obtained by non-thermodynamic means.

The thermodynamic ("low-frequency") theory of fluctuations leads to a different expression (see, for example[10]):

$$\overline{(\Delta p)^2} = -kT(\partial p/\partial V)_S \qquad (30)$$

(see critical remarks concerning (30) in[11]). For an ideal gas, calculations by means of formulas (29) and (30) yield respectively

$$\overline{(\Delta p)^2}/p^2 = 2/3N, \qquad (31)$$

$$\overline{(\Delta p)^2}/p^2 = 5/3N. \qquad (32)$$

Formula (31) [which corresponds to (29)] coincides with the formula of Munster[11].

The difference between (29) and (30) is essential also for liquids with noticeable dispersion of the speed of sound, i.e., when $K_S(\infty) \neq K_S(0)$. For liquids of low viscosity, when the difference between $K_S(\infty)$ and $K_S(0)$ can be neglected, formulas (29) and (30) practically coincide (the second term in the right side of (29) can be neglected, for under normal conditions we have for liquids $p/K_S \sim 10^{-4}$).

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