DERIVATION OF THE EQUATIONS

OF LINEAR VISCOELASTICITY

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In the last decade a new idea has been introduced into the statistical the-ory irreversible processes, an idea which, in particular, permits the deri-vation of the hydrodynamic equations and of expressions for the hydrodynamic transport coefficients, giving in principle the possibility of their calcu-lation on the basis of molecular models (cf., for example, [1]). In the pre-sent paper equations connecting the stress with small deformations of a vis-coelastic body are derived in a similar way.

External forces, acting on a viscoelastic body, deform it and induce in it flow processes characterized by a velocity distribution $v(x,t)$ (x is the position vector); that is, these forces bring about a state of thermodynamic inequilibrium in the body. The problem reduces to the determination of the statistical distribution of these nonequilibrium states. Generally the so-called local equilibrium distribution is taken as the zero approximation. This distribution is attained if the entire body is divided into "infinitesi-mal" but macroscopic elements of volume and if it is supposed that each ele-ment is in an equilibrium characterized by Gibbs' canonical distribution.

$$\rho_L = \exp\left\{\beta \int d^3x \, [F(x) - H^\circ(x)]\right\} \qquad \left(\beta = \frac{1}{kT}\right) \qquad (1)$$

Here k is the Boltzmann constant, T the absolute temperature, $F(x,t)$ the free energy density, and $H^\circ(x)$ the Hamiltonian density in a system of coordinates moving with velocity $v(x,t)$; the intergration is extended over the volume of the body.

The function $H^\circ(x)$ is connected with the Hamiltonian of the system H through the relation

$$\int H^\circ(x) \, d^3x = H - \sum_i p_i v_i + \frac{1}{2} \sum_i m_i v_i^2 \qquad (2)$$

where m_i and p_i are the mass and momentum of the ith particle, $v_i = v(r_i,t)$ is the value of the velocity at the location of the ith particle.

The external forces are not included in H. However, without loss of generality, it can be considered that the external forces have a potential Ф with explicit time dependence. Indeed, the molecules on the boundary of the body can be excluded from the system, and the forces of interaction between the molecules of the system and the molecules on the boundary, the coordinates of which represent external parameters, can be regarded as the external forces. Distribution (1) is the generalization to condensed media of the local equilibrium distribution introduced by Chapman and Enskog for ideal gases [2].

We write the exact distribution in the form

$$\rho = \exp{[\beta\ (l + c)]} \qquad (\beta\, l = \ln \rho_L) \tag{3}$$

Here c is a correction. The distribution must satisfy the Liouville equation

$$\frac{d\rho}{dt} = \frac{\partial\rho}{\partial t} + \{H + \Phi,\ \rho\} = 0$$

Substituting (3) into the above yields

$$dc\,/\,dt = -\,dl\,/\,dt \tag{4}$$

We will assume that the deformation process begins at the moment $t = 0$, that up to this moment the body is in an equilibrium undeformed state. With this $\sim$ reduces to the usual Gibbs distribution and $c = 0$. The symbolic solution to Equation (4) with initial condition $c = 0$ has the form

$$c\ (X_t,\ t) = -\int_0^t \frac{dl\ (X_\tau,\ \tau)}{d\tau}\,d\tau$$

where X_τ is the set of phase coordinates of the system at the moment τ.

We will restrict ourselves to the cases of small velocity gradient; that is, to weak nonequilibrium. The quantity c is a measure of the nonequilibrium of the system, and therefore distribution (3) can be expanded in the series

$$\rho = \rho_L\ (1 + \beta c + \ldots) \tag{5}$$

Assume that the Hamiltonian of the system has the form

$$H = \sum_k \left(\frac{p_k^{\,2}}{2m_k} + \varepsilon_k\right) + \sum_{k < l} u_{kl} \tag{6}$$

where ε_k is the internal energy of the particle, and u_{kl} is the interaction energy between the kth and lth particles. In the large majority of cases the force of intermolecular interaction has a limiting radius of interaction small in comparison with the scale of macroscopic inhomogeneities. With this condition the stress tensor $\sigma_{\alpha\beta}$ is obtained as the statistical mean of a tensor $-\Pi_{\alpha\beta}^{\,\circ}$, where

$$\Pi_{\alpha\beta}^{\,\circ} = \frac{1}{V}\left[\sum_i \frac{p_{i\alpha}^{\,\circ}p_{i\beta}^{\,\circ}}{m_i} - \sum_{i<j}(r_{i\alpha} - r_{j\alpha})\frac{\partial u_{ij}}{\partial r_{i\alpha}}\right] \qquad (\mathbf{p}_i^{\,\circ} = \mathbf{p}_i - m_i\mathbf{v}_i) \tag{7}$$

Here $\mathbf{p}_i^{\,\circ}$ is the momentum relative to a system of coordinates moving with velocity $\mathbf{v}(\mathbf{r}_i, t)$, V is some macroscopic volume, and the summation extends over the molecules in this volume (cf., for example, [3 and 4]).

From the definition ρ_L it follows that the tensor

$$\sigma_{\alpha\beta}^{\,\circ} = -\,\langle\Pi_{\alpha\beta}^{\,\circ}\rangle_L \tag{8}$$

where the angle brackets with subscript L signify an average with respect to the local equilibrium distribution, is determined by the deformations just as though the flow processes did not exist; i.e. is determined by the usual Hooke's law.

Averaging (7) with the aid of distribution (5) we get

$$\sigma_{\alpha\beta} = \sigma_{\alpha\beta}^{(0)} + \sigma_{\alpha\beta}^{(1)} + \ldots \qquad \left(\sigma_{\alpha\beta}^{(1)} = \beta\int_0^t dt'\left\langle\Pi_{\alpha\beta}^{\,\circ}(X_t),\ \frac{dl\ (X_\tau,\ \tau)}{d\tau}\right\rangle\right) \tag{9}$$

Quantities of the type $\langle A\ (X_t)\,B\ (X_\tau)\rangle$ are called temporal correlation functions and play a large role in contemporary theories of irreversible processes.

Now it is necessary to compute

$$\frac{dl}{dt} = \frac{\partial l}{\partial t} + \{H,\ l\} + \{\Phi,\ l\} \tag{10}$$

The effect of the interaction Φ on the motion in phase space of a macro-

scopic body, containing a large number of particles, is insignificant com-
pared with $H : \phi$ acts only on those particles near the boundary. Therefore
in the calculation (10) the third term on the right side can be neglected.
(This of course can be done if we examine the motion over an interval of time
small compared with the Poincaré cycle).

On the basis of (1), (2) and (6) we get, expanding out the Poisson brack-
ets,

$$\frac{dl}{dt} = \int d^3\mathbf{x}\, \frac{\partial F}{\partial t} + \sum_k \mathbf{p}_k{}^\circ \frac{\partial \mathbf{v}_k}{\partial t} + \sum_k \frac{p_{k\alpha} p_{k\beta}}{m_k} \frac{\partial v_{k\alpha}}{\partial r_{k\beta}} + \sum_{k+l} \frac{\partial u_{kl}}{\partial r_{k\alpha}} v_{k\alpha} - \sum_k v_{k\alpha} p_{k\beta} \frac{\partial v_{k\alpha}}{\partial r_{k\beta}} \qquad (11)$$

Here summation with respect to repeated Greek subscripts is implied.

Let us examine the term

$$\sum_{k+l} \frac{\partial u_{kl}}{\partial r_{k\alpha}} v_{k\alpha} = \frac{1}{2} \sum_{k+l} \frac{\partial u_{kl}}{\partial r_{k\alpha}} (v_{k\alpha} - v_{l\alpha}) \qquad (12)$$

As already mentioned, the radius of intermolecular interactions is much
smaller than the scale of macroscopic inhomogeneities, including inhomoge-
neities in the velocity. Therefore

$$v_{k\alpha} - v_{l\alpha} \approx -\frac{\partial v_{k\alpha}}{\partial r_{k\beta}} (r_{k\beta} - r_{l\beta}) \qquad (13)$$

The free energy density depends on the time through the time dependence
of the components of the deformation tensor; that is

$$\partial F / \partial t = (\partial F / \partial u_{\alpha\beta})(\partial u_{\alpha\beta} / \partial t).$$

From (8) follows

$$\partial F / \partial u_{\alpha\beta} = \sigma_{\alpha\beta}^\circ \qquad (14)$$

In addition,

$$\frac{\partial u_{\alpha\beta}}{\partial t} = \frac{1}{2}\left(\frac{\partial v_\alpha}{\partial x_\beta} + \frac{\partial v_\beta}{\partial x_\alpha}\right) \qquad (15)$$

Substitution of (12) — (15) into (11) yields

$$\frac{dl}{dt} = \int \sigma_{\alpha\beta}^{(0)} \frac{\partial v_\alpha}{\partial x_\beta} d^3\mathbf{x} + \sum_k \mathbf{p}_k{}^\circ \frac{\partial \mathbf{v}_k}{\partial t} + \sum_k (\Pi_{k\alpha\beta} - v_{k\alpha} p_{k\beta}) \frac{\partial v_{k\alpha}}{\partial r_{k\beta}} \qquad (16)$$

Here

$$\Pi_{k\alpha\beta} = \frac{p_{k\alpha} p_{k\beta}}{m_k} - \frac{1}{2} \sum_l \frac{\partial u_{kl}}{\partial r_{k\alpha}} (r_{k\beta} - r_{l\beta})$$

We will neglect all terms of higher order in the velocity gradients. Then

$$\frac{\partial v_{k\alpha}}{\partial t} \approx - v_{k\beta} \frac{\partial v_{k\alpha}}{\partial r_{k\beta}}$$

which allows us to write (16) in the form

$$\frac{dl}{dt} = \int \sigma_{\alpha\beta}^\circ \frac{\partial v_\alpha}{\partial x_\beta} d^3\mathbf{x} - \sum_k (\Pi_{k\alpha\beta} - v_{k\alpha} p_{k\beta} - p_{k\alpha}^{(0)} v_{k\beta}) \frac{\partial v_{k\alpha}}{\partial r_{k\beta}} \qquad (17)$$

As a system we can consider any sufficiently large volume of the body. In
the case of small gradients it is possible to choose such a volume V that
the velocity gradient in it is constant. Then (17) takes the form

$$\frac{dl}{dt} = T_{\alpha\beta} \frac{\partial v_\alpha}{\partial x_\beta} \qquad \left(T_{\alpha\beta} = V\Pi_{\alpha\beta}^\circ + \int_V \sigma_{\alpha\beta}^{(0)} d^3\mathbf{x}\right) \qquad (18)$$

Substitution of (18) into (9) yields

$$\sigma_{\alpha\beta}^{(1)} = \frac{1}{kT} \int_0^t d\tau \, \langle \Pi_{\alpha\beta}^\circ (X_t) T_{\mu\nu}(X_\tau)\rangle_L \frac{\partial v_\mu(\tau)}{\partial X_\nu} \qquad (19)$$

From (8) it follows that $\langle T_{\mu\nu}\rangle_L = 0$, therefore relation (19) can be put in more symmetrical form

$$\sigma_{\alpha\beta}^{(1)} = \frac{1}{kTV} \int\limits_0^t d\tau \, \langle T_{\alpha\beta}\,(X_t)\, T_{\mu\nu}\,(X_\tau)\rangle_L \frac{\partial v_\mu\,(\tau)}{\partial X_\nu} \tag{20}$$

Integrating (20) by parts and taking account of (15) and the fact that $u_{\mu\nu}\,(0) = 0$, we get finally

$$\sigma_{\alpha\beta}^{(1)} = \frac{1}{kTV}\, \langle T_{\alpha\beta} T_{\mu\nu}\rangle_L\, u_{\mu\nu}\,(t) - \int\limits_0^t K_{\alpha\beta\mu\nu}\,(t-\tau)\, u_{\mu\nu}\,(\tau)\, d\tau \tag{21}$$

Here

$$K_{\alpha\beta\mu\nu} = \frac{1}{kTV} \frac{d}{d\tau}\, \langle T_{\alpha\beta}\,(X_t)\, T_{\mu\nu}\,(X_\tau)\rangle_L \tag{22}$$

Due to the short-range character of the intermolecular force the elastic coefficients and functions in (21), as must be the case, do not depend on the volume V.

Adding $\sigma_{\alpha\beta}^{(0)}$ and $\sigma_{\alpha\beta}^{(1)}$, we see that the first term on the right-hand side of (21) leads only to a change in the coefficients of Hooke's law, while the second term expresses the hereditary property of the medium. As a result we have

$$\sigma_{\alpha\beta} = \lambda_{\alpha\beta\mu\nu} u_{\mu\nu} - \int\limits_0^t K_{\alpha\beta\mu\nu}\,(t-\tau)\, u_{\mu\nu}\,(\tau)\, d\tau \tag{23}$$

Equation (23) is a known relation of linear viscoelasticity (cf., for example, [5 and 6]), which is derived here on the basis of general principles of statistical physics, with practically the only modelling assumption being contained in the assumption of the redius of action of the intermolecular force. However, in order to calculate, with the aid of relation (22), the relaxation coefficients, all details of the model will of course be necessary. It is necessary to point out that the anisotropy of $K_{\alpha\beta\mu\nu}$ may be brought about by both the anisotropy of the medium and of the deformation. In other words the anisotropy of $\lambda_{\alpha\beta\mu\nu}$ and $K_{\alpha\beta\mu\nu}$ may be different in magnitude.

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Translated by W.T.S.