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Abstract

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HYDROMECHANICS

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ON THE MACROSCOPIC DESCRIPTION OF KINETIC PROCESSES

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The presence of small parameters in the equations of kinetics makes it possible to divide the relaxation process into a "fast" and a "slow" one (^{1}). In describing the "slow" process one has to make hypotheses concerning the form of the distribution function. The purpose of the present note is to give a uniform scheme for introducing such hypotheses, in which the macroscopic quantities that determine the "slow" motion are assumed to be already known.

Among the quantities singled out there may be "relaxing" (vanishing in equilibrium) quantities, such as the heat flux, the tensor of viscous stresses, etc.; moreover, in contrast to the thermodynamics of irreversible processes, they are regarded as independent, so that differential equations of motion are also formulated for the "nonequilibrium" quantities (similarly to what was done in (^{2})).

1°. Let us divide the layer of the phase space of the system adjacent to the surface of a given energy into cells $R(f, \Delta f)$, corresponding to the values $f_1, \dots, f_n$ (with certain tolerances $\Delta f_1, \dots, \Delta f_n$) of the selected quantities $F_1(\Omega), \dots, F_n(\Omega)$, functions of the phase point Ω. Suppose that over a time $\sim \tau$ a microscopically negligibly small fraction of the phase volume flows out of the cells $R(f, \Delta f)$, by virtue of the dynamical equations. Assume that there exists a time interval $\theta \ll \tau$, during which the ensemble in each of the cells $R(f, \Delta f)$ has time to become distributed approximately uniformly over the cell. Then, in describing the "slow" process of change of the probability distribution $w(f_1, \dots, f_n, t)$ of the values of the selected quantities $F_1(\Omega), \dots, \dots, F_n(\Omega)$, one may assume that the ensemble of microsystems has the form

$$\Psi(\Omega, t) = \Phi[F_1(\Omega), \dots, F_n(\Omega), t], \tag{1}$$

and

$$w(f_1, \dots, f_n, t) = \Gamma(f_1, \dots, f_n)\Phi(f_1, \dots, f_n, t), \tag{2}$$

where $\Gamma(f_1, \dots, f_n)\Delta f_1 \cdots \Delta f_n$ is the volume of the cell $R(f, \Delta f)$. A strong deviation from the statistical hypothesis (1) would mean that specifying $w(f_1, \dots, \dots, f_n, t)$ does not even approximately determine the further course of the process, and that other physical quantities should be chosen as the determining ones. The possibility of a Markov description of kinetic processes, connected with "intermediate" mixing over cells, was pointed out by N. S. Krylov (^{3}).

Separating in the Hamiltonian of the system the "sharp" interactions (collisions) with characteristic time $< \theta$, we introduce functions $\lambda(f/f')$ and $V_k(f)$ such that

$$\Gamma(f)\Delta f_1 \cdots \Delta f_n\, \lambda(f/f')\Gamma(f')\Delta f_1' \cdots \Delta f_n'$$

is the phase volume passing per unit time from $R(f', \Delta f')$ into $R(f, \Delta f)$ owing to collisions, while ΓV_k is the density of the continuous flux of phase volume through the surface of the image of the cell in the space of values $(f_1, \dots, f_n)$. By reversibility of collisions, $\lambda(f/f') = \lambda(f'/f)$, and, by Liouville' s theorem,

$$\sum_k \frac{\partial \Gamma V_k}{\partial f_k} = 0.$$

Writing the balance of the number of microsystems of the ensemble, one can, with the aid of (1), obtain the evolution equation

$$\frac{\partial w}{\partial t} + \sum_k \frac{\partial w V_k}{\partial f_k} = \int \lambda\left(\frac{f}{f'}\right)\left[\frac{w(f')}{\Gamma(f')} - \frac{w(f)}{\Gamma(f)}\right]\Gamma(f)\Gamma(f')\, df_1' \cdots df_n'. \tag{3}$$

The entropy of the ensemble

$$H = -k \int w \ln \frac{w}{\Gamma}\, df_1 \dots df_n$$

(where k is Boltzmann' s constant), by virtue of (3), does not decrease.

2°. In those cases where the characteristic time T of sufficiently small change of the mean values $\bar{f}_1, \dots, \bar{f}_n$ is much greater than τ, one may assume that in the "slow" process of evolution of the mean values the ensemble of microsystems (and hence $w(f, t)$) is determined only by these means. If, moreover, one assumes that the entropy H, which increases by virtue of (3), has time during the interval T to grow to the maximum value compatible with the values of the means in this interval, then we arrive at the statistical hypothesis of an ensemble of maximum entropy:

$$w(f,t) = C\Gamma(f)\exp\left[-\frac{1}{k}\sum_i \alpha_i f_i\right], \tag{4}$$

where the parameters C and α_i are determined by the mean values and by the normalization condition. The entropy H of the ensemble (4) satisfies the condition

$$\partial H/\partial \bar{f}_i = \alpha_i. \tag{5}$$

Introducing the conjugate physical quantities $g_i = \partial k \ln \Gamma(f)/\partial f_i$, we easily obtain $\bar{g}_i = \alpha_i$ and the relation for fluctuations $\overline{(g_i - \bar{g}_i)^2}\,\overline{(f_i - \bar{f}_i)^2} \geq k^2$.

Using the statistical hypothesis (4), with the aid of (3) we obtain a closed system of equations for the change of the means:

$$\frac{d\bar{f}_i}{dt} = \int C\Gamma V_i \exp\left[-\frac{1}{k}\sum_s \alpha_s f_s\right] df_1 \dots df_n + \frac{1}{2}\int C\lambda\left(\frac{f}{f'}\right)\Gamma(f)\Gamma(f')(f_i - f_i')\times$$
$$\times\left(\exp\left[-\frac{1}{k}\sum_s \alpha_s f_s'\right] - \exp\left[-\frac{1}{k}\sum_s \alpha_s f_s\right]\right) df_1 \dots df_n\, df_1' \dots df_n'. \tag{6}$$

3°. Near equilibrium, for the entropy of the ensemble (4) we obtain

$$H = H_0 - \frac{1}{2}\sum_{i,j} D_{ij}\Delta\bar{f}_i\,\Delta\bar{f}_j, \tag{7}$$

where H_0 is the equilibrium entropy, $\Delta\bar{f}_i$ is the deviation of the means from their equilibrium values, and D_{ij} is a positive definite matrix.

Linearization of (6) gives

$$\frac{d\Delta\bar{f}_i}{dt} = -\sum_s A_{is}\alpha_s + \sum_s B_{is}\alpha_s, \tag{8}$$

where the antisymmetric matrix A_{is} is associated with the flow terms, the symmetric nonnegative matrix B_{is} is due to collisions, and

$$\alpha_s = -\sum_r D_{sr}\Delta\bar{f}_r.$$

If the quantity F_i is an invariant of collisions, then $B_{is} = B_{si} = 0$. Therefore the production of entropy

$$\frac{dH}{dt} = \sum_{i,s} B_{is} \alpha_i \alpha_s \geq 0$$

depends only on the conjugate parameters of the remaining (“relaxing”) quantities. It is easy to show that, by a linear redefinition of the “relaxing” quantities, one can arrange that the latter be expressed only through their conjugate parameters. Then it turns out that, by virtue of (8), the means of the relaxing quantities go to zero (which, generally speaking, is not true for invariants of collisions).

Let the integral in (3) contain a large parameter $1/\varepsilon$ (“many collisions”). Then after a time $t \sim \varepsilon$, by virtue of (8), the conjugate parameters of the relaxing quantities are expressed linearly through the conjugate parameters of the invariants of collisions. This relation makes it possible to derive all cor—

relations of the thermodynamics of irreversible processes, with the “forces” being the conjugate parameters of the collision invariants. As a result of eliminating the relaxing conjugate parameters, irreversible terms (due to collisions) appear in the equations for the collision invariants; these play the role of Onsager “fluxes.”

It is important to emphasize that the collision invariants and the relaxing quantities are independent, and only because of the large number of collisions is a connection established between them, and with it the relations of the thermodynamics of irreversible processes.

4°. In a continuous medium (for example, in a rarefied gas) a set of local additive physical quantities is specified in the form

$$F_{j,\mathbf{X}} = \sum_{i=1}^{N} h_j(\mathbf{x}_i, \mathbf{p}_i)\, \delta(\mathbf{x}_i - \mathbf{X}), \qquad j = 1, 2, \dots, m, \tag{9}$$

where $\mathbf{x}_i, \mathbf{p}_i$ are canonical variables, the discrete index j distinguishes physical quantities of different nature, and the continuous vector index $\mathbf{X}$ denotes their local values.

Denoting the conjugate parameters by $\alpha_j(\mathbf{X})$, we write the maximum-entropy ensemble for (9), in accordance with (4), in the form

$$\Phi = C \exp\left\{ -\frac{1}{k} \sum_{j=1}^{m} \sum_{i=1}^{N} \alpha_j(\mathbf{x}_i)\, h_j(\mathbf{x}_i, \mathbf{p}_i) \right\}. \tag{10}$$

Bearing in mind that the ensemble (10) is concentrated in the layer adjacent to the prescribed value E of the system energy, we obtain, for the probability density of finding the microsystem at the point $(\mathbf{x}_1, \dots, \mathbf{p}_N)$ of phase space,

$$\mathcal{P}(\mathbf{x}_1, \dots, \mathbf{p}_N) = \frac{\prod_{i=1}^{N} \varphi(\mathbf{x}_i, \mathbf{p}_i)\, \Delta \left[\sum_{i=1}^{N} \varepsilon(\mathbf{x}_i, \mathbf{p}_i) - E \right]}{\int \prod_{i=1}^{N} \varphi(\mathbf{x}_i, \mathbf{p}_i)\, \Delta \left[\sum_{i=1}^{N} \varepsilon(\mathbf{x}_i, \mathbf{p}_i) - E \right] \, d\mathbf{x}_1 \dots d\mathbf{p}_N}, \tag{11}$$

where

$$\varphi(\mathbf{x}_i, \mathbf{p}_i) = \exp \left\{ -\frac{1}{k} \sum_{j=1}^{m} \alpha_j(\mathbf{x}_i)\, h_j(\mathbf{x}_i, \mathbf{p}_i) \right\},$$

Δ is the characteristic function of the interval $(E, E + \Delta E)$, and $\varepsilon(\mathbf{x}_i, \mathbf{p}_i)$ is the energy of the i-th particle.

Assuming that among the quantities (9) there are the local energy and density ($h_1 \equiv 1$, $h_2 \equiv \varepsilon(\mathbf{x}, \mathbf{p})$), one can, from (11), using a modification of A. Ya. Khinchin' s method (^{4}), obtain the asymptotic (as $N \to \infty$, $E/N = \text{const}$) expression for the one-particle distribution function

$$\mathcal{P}_1(\mathbf{x}, \mathbf{p}) = \exp \left\{ \frac{1}{k\vartheta(\mathbf{x})} [\mu(\mathbf{x}) - \varepsilon(\mathbf{x}, \mathbf{p})] - \frac{1}{k} \sum_{r=3}^{m} \alpha_r(\mathbf{x})\, h_r(\mathbf{x}, \mathbf{p}) \right\}, \tag{12}$$

where $\vartheta(\mathbf{x})$, $\mu(\mathbf{x})$, and $\alpha_r(\mathbf{x})$, $r = 3, \dots, m$, are expressed through the mean values $\bar{f}_j(\mathbf{X})$ of the quantities (9) by means of the relations

$$N \int \mathcal{P}_1(\mathbf{x}, \mathbf{p})\, h_j(\mathbf{x}, \mathbf{p})\, d\mathbf{p} = \bar{f}_j(\mathbf{x}), \qquad j = 1, \dots, m. \tag{13}$$

At equilibrium ($\alpha_r = 0$), (12) becomes the Boltzmann distribution. In nonequilibrium states the temperature ϑ and chemical potential μ depend on all $\bar{f}_j$ (and not only on $\bar{f}_1$ and $\bar{f}_2$). However, near equilibrium this dependence on the relaxing quantities manifests itself only in second order. It can be shown that, for the ensemble (10), the entropy is asymptotically equal to

$$H = \int H(\mathbf{x})\, d\mathbf{x}, \quad \text{where}$$

$$H(\mathbf{x}) = -kN \int \mathcal{P}_1(\mathbf{x}, \mathbf{p}) \ln \mathcal{P}_1(\mathbf{x}, \mathbf{p})\, d\mathbf{p} \tag{14}$$

is the local entropy. It is easy to see that (12) provides the maximum of $H(\mathbf{x})$ under the conditions (13). Thus, the assumption of an ensemble of maximentropy (10) leads to a generalization to nonequilibrium states of Boltzmann' s principle of entropy maximization in μ-space.

Since the means (13) of additive physical quantities are determined only by the one-particle distribution function (12), in deriving dynamical equations for the means one may use, as an intermediate step, the kinetic equation

$$\frac{\partial \mathcal{P}_1}{\partial t} + \frac{\mathbf{p}}{m}\frac{\partial \mathcal{P}_1}{\partial \mathbf{x}} - \frac{\partial U}{\partial \mathbf{x}}\frac{\partial \mathcal{P}_1}{\partial \mathbf{p}} = J, \tag{15}$$

where J is the collision integral. Let us note that (15) is an equation for the mean values of the occupation numbers

$$N_{\mathbf{X},\mathbf{P}} = \sum_{i=1}^{N} \delta(\mathbf{x}_i - \mathbf{X})\delta(\mathbf{p}_i - \mathbf{P})$$

in μ-space, and the assumption of a maximum-entropy ensemble for $N_{\mathbf{X},\mathbf{P}}$ is precisely the "molecular chaos hypothesis" usually used in deriving (15).

As an example, let us consider viscous processes. A nonequilibrium viscous process in a monatomic gas is characterized by the densities of mass and momentum and by the momentum-flux tensor

$$\rho = \int f(\mathbf{x},\mathbf{v})\,d\mathbf{v}, \quad \rho u^{\nu} = \int v^{\nu} f(\mathbf{x},\mathbf{v})\,d\mathbf{v}, \quad p^{\mu\nu} + \rho u^{\mu}u^{\nu} = \int v^{\mu}v^{\nu} f(\mathbf{x},\mathbf{v})\,d\mathbf{v}, \tag{16}$$

where $\mathbf{v} = \mathbf{p}/m,\ f = mN\mathcal{P}_1$. The entropy maximum under the conditions (16) is attained for the distribution

$$f(\mathbf{x},\mathbf{v}) = \frac{\rho(\mathbf{x})}{(2\pi)^{3/2}}\sqrt{\frac{\rho^3}{\det\|p^{\mu\nu}\|}}\times$$

$$\times \exp\left\{-\frac{1}{2}\rho\, p_{\mu\nu}(v^{\mu}-u^{\mu})(v^{\nu}-u^{\nu})\right\} \quad (p^{ik}p_{kl} = \delta^{i}_{l}). \tag{17}$$

Using (17), with the aid of (15), one readily obtains a closed system of equations for the moments (16)

$$\frac{\partial \rho}{\partial t} + \frac{\partial \rho u^{\nu}}{\partial x^{\nu}} = 0, \quad \frac{\partial \rho u^{\nu}}{\partial t} + \frac{\partial(\rho^{\mu\nu} + \rho u^{\nu}u^{\mu})}{\partial x^{\mu}} + \frac{\rho}{m}\frac{\partial U}{\partial x^{\nu}} = 0,$$

$$\frac{\partial(p^{\nu\mu} + \rho u^{\nu}u^{\mu})}{\partial t} + \frac{\partial(\rho u^{\nu}u^{\mu}u^{\sigma} + p^{\mu\nu}u^{\sigma} + p^{\nu\sigma}u^{\mu} + p^{\mu\sigma}u^{\nu})}{\partial x^{\sigma}} + \frac{\rho u^{\nu}}{m}\frac{\partial U}{\partial x^{\mu}} + \frac{\rho u^{\mu}}{m}\frac{\partial U}{\partial x^{\nu}} +$$

$$+\frac{p}{\eta}\left(p^{\mu\nu}-\frac{1}{3}p^{\sigma\sigma}\delta^{\mu\nu}\right)=0, \qquad (18)$$

where η is the viscosity coefficient. System (18) coincides with the system that can be obtained by Grad' s method (^{2}) in the 10-moment approximation*. The 10-moment distribution in Grad' s method is the first term of the expansion of (18) in $\sigma^{\mu\nu}$. The entropy of the distribution (17) increases by virtue of (18).

In a polyatomic gas, when only processes of second viscosity are taken into account, one should prescribe the densities of mass, momentum, translational energy, and internal energy. The maximum-entropy distribution with respect to these quantities coincides with Kirkwood' s hypothesis (^{5}), and the equation for the means coincides with the well-known relaxation equations of gas dynamics.

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* For non-Maxwellian molecules, in (18) the nonlinear terms in $\sigma^{\mu\nu}=p^{\mu\nu}-p\delta^{\mu\nu}$ ($p=\frac{1}{3}p^{\sigma\sigma}$) are not taken into account; moreover, even the quadratic terms obtained with the aid of (17) differ from Grad' s.

Note: Figure translations are in progress. See original paper for figures.

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