ON THE THEORY OF TRANSPORT PHENOMENA IN DENSE MEDIA

1968

SovietRxiv

Abstract

Full Text

UDC 532.7

PHYSICS

A. D. KHONKIN

ON THE THEORY OF TRANSPORT PHENOMENA IN DENSE MEDIA

(Presented by Academician N. N. Bogolyubov, 23 IV 1968)

In deriving the transport laws and expressions for kinetic coefficients in isotropic dense media by methods of nonequilibrium statistical mechanics, it is assumed ([1,2]) that the macroscopic state of the system can be determined using a locally equilibrium distribution ρ_l, which is chosen as the first term in the expansion of the nonequilibrium distribution ρ in a series in the inhomogeneity parameter μ (in the gradients of the macroscopic variables). Then one may consider that, for the macroscopic variables, which are functions of coordinates and time, the relations valid in equilibrium thermodynamics hold, and construct the next term of the expansion ρ_1, linear in μ. To justify this assumption it is necessary to show that the contribution to the mean values of the dynamic variables of the number densities of particles $\hat{n}_k(r)$, momentum $\hat{p}_\alpha(r)$, and energy $\hat{e}(r)$ from the function ρ_1 is equal to zero. It is shown below that these questions are closely connected with other interesting properties of a nonequilibrium system. The vanishing of the contributions to the mean values of $n_k(\hat{r})$ and $\hat{e}(r)$ is connected with nonlocal fluctuation relations and is a consequence of the fact that the density of the thermodynamic potential p (pressure) is a function of state. The vanishing of the contribution to the mean value $\hat{p}_\alpha(r)$ follows from Onsager' s theorem on the equality of (nonlocal) cross kinetic coefficients. The method of the nonequilibrium ensemble of D. N. Zubarev ([4]) is used in the work.

1. Consider a system of N classical structureless molecules of L different species. We shall start from the equations

$$\dot{\hat{n}}_k(r) + \partial_\alpha \hat{j}_{k\alpha}(r) = 0; \qquad \dot{\hat{p}}_\alpha(r) + \partial_\beta \hat{p}_{\alpha\beta}(r) = 0; \qquad \dot{\hat{e}}(r) + \partial_\alpha \hat{q}_\alpha(r) = 0, \quad (1)$$

where $\hat{j}_{k\alpha}(r)$, $\hat{p}_{\alpha\beta}(r)$, $\hat{q}_\alpha(r)$ are dynamic variables of the densities of the fluxes of the corresponding quantities ([1]). The nonstationary Gibbs ensemble has the form ([4])

$$\rho(x_1, \dots, x_N; t) = Q^{-1} \exp\left\{ -\sum_s \int B_s(r', t)\, dr' \right\}, \tag{2}$$

where $B_s(r,t)$ are local quasi-integrals of motion constructed on the basis of equations (1):

$$B_s(r,t) = F_s(r,t)\hat{P}_s(r) -$$

$$-\int_{-\infty}^{0} \exp(\varepsilon t_1) \left[F_s(r, t+t_1)\dot{\hat{P}}_s(r, t_1) + \frac{\partial F_s(r, t+t_1)}{\partial t_1} \hat{P}_s(r, t_1) \right] dt_1. \tag{3}$$

Here $\hat{P}_k(r) = \hat{n}_k(r)$, $F_k(r,t) = -(\nu_k(r,t) - \frac{1}{2}\beta(r,t) m_k u^2(r,t))$, $k = 1, \dots, L$, $\hat{P}_{L+\alpha}(r) = \hat{p}_\alpha(r)$, $F_{L+\alpha}(r,t) = -\beta(r,t) u_\alpha(r,t)$, $\alpha = 1, 2, 3$; $\hat{P}_{L+4}(r) = \hat{e}(r)$, $F_{L+4}(r,t) = \beta(r,t)$; β is the inverse temperature, $\nu_k = \beta\mu_k$; μ_k is the chemical potential; u is the mass velocity; $\hat{P}_s(r,t) = \exp(tH_N)\hat{P}_s(r)$, where $\exp(tH_N)$ is the evolution operator. The limiting transition $\varepsilon \to 0$ should be performed after letting the volume of the system tend to infinity.

Let us replace $\dot{\hat{P}}_s(r)$ in (3) according to equations (1) and integrate by parts the terms with derivatives of the dynamic variables, neglecting surface integrals. Expanding the resulting function ρ in gradients of the macroscopic variables, in the linear approximation we have

$$\rho = \rho_l(1 + \Delta\rho), \tag{4}$$

where

$$\rho_l = Q_l^{-1} \exp\left\{ -\sum_s \int F_s(r', t)\hat{P}_s(r')\, dr' \right\}; \tag{5}$$

$$\begin{aligned} \Delta\rho = -\int dr' \int_{-\infty}^{0} dt_1 \exp(\varepsilon t_1) \Bigg[& \sum_{k=1}^{L} \hat{I}_{k\alpha}(r', t_1)\partial_\alpha v_k(r', t+t_1) \\ & + \hat{S}_\alpha(r', t_1)(-\partial_\alpha \beta(r', t+t_1)) + \frac{1}{2}\beta\hat{\Pi}_{\alpha\beta}(r', t_1) D_{\alpha\beta}(r', t+t_1) \\ & + \frac{1}{3}\beta\widetilde{\Pi}_{\alpha\alpha}(r', t_1)\partial_\beta u_\beta(r', t+t_1) \Bigg]; \end{aligned} \tag{6}$$

$$\hat{I}_{k\alpha}(r) = \hat{J}_{k\alpha}(r) - (n_k/\rho)\hat{P}_\alpha(r), \qquad \hat{S}_\alpha(r) = \hat{Q}_\alpha(r) - (h/\rho)\hat{P}_\alpha(r),$$

$$\hat{\Pi}_{\alpha\beta}(r) = \hat{P}_{\alpha\beta}(r) - \frac{1}{3}\delta_{\alpha\beta}\hat{P}_{\gamma\gamma}(r); \qquad D_{\alpha\beta} = \partial_\alpha u_\beta + \partial_\beta u_\alpha - \frac{2}{3}\delta_{\alpha\beta}\partial_\gamma u_\gamma,$$

$$\frac{1}{3}\widetilde{\Pi}_{\alpha\alpha}(r) = \frac{1}{3}\widetilde{P}_{\alpha\alpha}(r) - p - \left(\frac{\partial p}{\partial E}\right)_{n_k}(\hat{E}(r) - E) - \sum_{k=1}^{L}\left(\frac{\partial p}{\partial n_k}\right)_{E,n_k'}(\hat{n}_k(r) - n_k); \tag{7}$$

ρ is the mass density; $h = E + p$ is the enthalpy density. Dynamic variables in a coordinate system moving with the local velocity of the medium (replacement of momenta p_i by "thermal momenta" $p_i - m_i u$) are denoted by capital letters, and their mean values by the same letters but without a hat above.

In deriving expression (6), to replace the derivatives $\partial F_s/\partial t$, the hydrodynamic equations of the first approximation were used; these can be obtained by averaging equations (1) over ρ_l, as well as the transition formulas to the moving coordinate system for the dynamic variables.

2. Using formula (6), we obtain expressions for the mean fluxes in the linear approximation, i.e., the transport laws

$$J_{k\alpha}(r,t) = -\int dr' \int_{-\infty}^{0} dt_1 \exp(\varepsilon t_1)\left[\sum_{k'=1}^{L} D_{kk'}(r,r',t_1)\partial_\alpha v_{k'}(r',t+t_1) + \widetilde{D}_k^T(r,r',t_1)(-\partial_\alpha \beta(r',t+t_1))\right],$$

$$\Pi_{\alpha\beta}(r,t) = -\int dr' \int_{-\infty}^{0} dt_1 \exp(\varepsilon t_1)\left[\eta(r,r',t_1)D_{\alpha\beta}(r',t+t_1) + \eta_V(r,r',t_1)\partial_\gamma u_\gamma(r',t+t_1)\delta_{\alpha\beta}\right], \tag{8}$$

$$Q_\alpha(r,t) = -\int dr' \int_{-\infty}^{0} dt_1 \exp(\varepsilon t_1)\left[kT^2\lambda(r,r',t_1)(-\partial_\alpha \beta(r',t+t_1)) + \sum_{k=1}^{L} D_k^T(r,r',t_1)\partial_\alpha v_k(r',t+t_1)\right],$$

where

$$D_{kk'}(r,r',t_1) = \frac{1}{3}\langle \hat{J}_{k\alpha}(r)\hat{I}_{k'\alpha}(r',t_1)\rangle_l,$$

$$\widetilde{D}_k^T(r,r',t_1) = \frac{1}{3}\langle \hat{J}_{k\alpha}(r)\hat{S}_\alpha(r',t_1)\rangle_l,$$

$$D_k^T(r,r',t_1) = \frac{1}{3}\langle \hat{Q}_\alpha(r)\hat{I}_{k\alpha}(r',t_1)\rangle_l,$$

$$\eta(r,r',t_1) = (\beta/10)\langle \hat{P}_{\alpha\beta}(r)\hat{\Pi}_{\alpha\beta}(r',t_1)\rangle_l, \tag{9}$$

$$\eta_V(r,r',t_1) = (\beta/9)\langle \hat{P}_{\alpha\alpha}(r)\widetilde{\Pi}_{\alpha\alpha}(r',t_1)\rangle_l,$$

$$\lambda(r,r',t_1) = (\beta^2/3k)\langle \hat{Q}_\alpha(r)\hat{S}_\alpha(r',t_1)\rangle_l$$

are the correlators of the kinetic coefficients, and the index l denotes averaging over ρ_l.

Formulas (9) were obtained by another method by McLennan ([2]), and also by Kadanoff and Martin ([3]), in whose work, however, the averaging is performed over the equilibrium ensemble and a one-component medium is considered. Note that in formulas (8) all macroscopic variables are functions of the point r' and time $t + t_1$.

3. One of the essential requirements of the theory is the fulfillment of the relations

$$n_k(r,t) = \langle \hat{n}_k(r)\rangle_l, \qquad \rho(r,t)u_\alpha(r,t) = \langle \hat{p}_\alpha(r)\rangle_l, \qquad e(r,t) = \langle \hat{e}(r)\rangle_l, \tag{10}$$

which mean that the parameters of the macroscopic state can be determined with the aid of the function ρ_l alone. Using the linear approximation, we reduce relations (10) to the form

$$\int dr' \int_{-\infty}^{0} dt_1 \exp(\varepsilon t_1)\beta(r',t+t_1)\langle \hat{n}_k(r)\tilde{\Pi}_{\alpha\alpha}(r',t_1)\rangle_l \partial_\gamma u_\gamma(r',t+t_1) = 0,$$

$$\int dr' \int_{-\infty}^{0} dt_1 \exp(\varepsilon t_1)\beta(r',t+t_1)\langle \hat{E}(r)\tilde{\Pi}_{\alpha\alpha}(r',t_1)\rangle_l \partial_\gamma u_\gamma(r',t+t_1) = 0,$$

$$\int dr' \int_{-\infty}^{0} dt_1 \exp(\varepsilon t_1)\left[\langle \hat{P}_\alpha(r)\hat{S}_\alpha(r',t_1)\rangle_l(-\partial_\beta\beta(r',t+t_1)) + \right.$$

$$\left. + \sum_{k=1}^{L}\langle \hat{P}_\alpha(r)\hat{I}_{k\alpha}(r',t_1)\rangle_l \partial_\beta \nu_k(r',t+t_1)\right] = 0,$$

or, owing to the independence of the thermodynamic forces, to the form

$$\left\langle \hat{n}_k(r) \left[\frac{1}{3}\hat{P}_{\alpha\alpha}(r', t_1) - p - \left(\frac{\partial p}{\partial E}\right)_{n_k} (\hat{E}(r', t_1) - E) - \sum_{k=1}^{L} \left(\frac{\partial p}{\partial n_k}\right)_{E, n'_k} (\hat{n}_k(r', t_1) - n_k) \right] \right\rangle_l = 0; \tag{11a}$$

$$\left\langle \hat{E}(r) \left[\frac{1}{3}\hat{P}_{\alpha\alpha}(r', t_1) - p - \left(\frac{\partial p}{\partial E}\right)_{n_k} (\hat{E}(r', t_1) - E) - \sum_{k=1}^{L} \left(\frac{\partial p}{\partial n_k}\right)_{E, n'_k} (\hat{n}_k(r', t_1) - n_k) \right] \right\rangle_l = 0; \tag{11b}$$

$$\left\langle \hat{P}_\alpha(r) \left[\hat{Q}_\alpha(r', t_1) - (h/\rho)\hat{P}_\alpha(r', t_1) \right] \right\rangle_l = 0, \tag{12a}$$

$$\left\langle \hat{P}_\alpha(r) \left[\hat{I}_{k\alpha}(r', t_1) - (n_k/\rho)\hat{P}_\alpha(r', t_1) \right] \right\rangle_l = 0. \tag{12b}$$

Varying the definition of the mean value $P_i(r', t + t_1) = \langle \hat{P}_i(r', t_1) \rangle_l$, we obtain fluctuation relations in the locally equilibrium ensemble

$$[\delta P_i(r', t + t_1)/\delta F_s(r, t)]_{F'_s} = \left\langle \left[\hat{P}_s(r) - P_s(r, t) \right] \hat{P}_i(r', t_1) \right\rangle_l =$$

$$= \left\langle \hat{P}_s(r) \left[P_i(r', t_1) - P_i(r', t + t_1) \right] \right\rangle_l . \tag{13}$$

Using these relations, (11) can be rewritten in the form of nonlocal thermodynamic identities

$$\left(\frac{\delta p(r', t + t_1)}{\delta \nu_k(r, t)}\right)_{\beta, \nu'_k} - \left(\frac{\delta p(r', t + t_1)}{\delta E(r', t + t_1)}\right)_{n_k} \left(\frac{\delta E(r', t + t_1)}{\delta \nu_k(r, t)}\right)_{\beta, \nu'_k} -$$

$$- \sum_{k'=1}^{L} \left(\frac{\delta p(r', t + t_1)}{\delta n_{k'}(r', t + t_1)}\right)_{E, n_k} \left(\frac{\delta n_{k'}(r', t + t_1)}{\delta \nu_k(r, t)}\right)_{\beta, \nu'_k} = 0; \tag{14a}$$

$$\left(\frac{\delta p(r', t + t_1)}{\delta \beta(r, t)}\right)_{\nu_k} - \left(\frac{\delta p(r', t + t_1)}{\delta E(r', t + t_1)}\right)_{n_k} \left(\frac{\delta E(r', t + t_1)}{\delta \beta(r, t)}\right)_{\nu_k} -$$

$$- \sum_{k=1}^{L} \left(\frac{\delta p(r', t + t_1)}{\delta n_k(r', t + t_1)}\right)_{E, n_k} \left(\frac{\delta n_k(r', t + t_1)}{\delta \beta(r, t)}\right)_{\nu_k} = 0. \tag{14b}$$

Relations (14) assert that the density of the thermodynamic potential $p(r,t)$ is a function of the state of the system described by the "parameters" $\nu_k(r,t)$, $\beta(r,t)$ (or $n_k(r,t)$ and $E(r,t)$).

Before proceeding to the analysis of relations (12), let us consider the symmetry relations for the correlators of the kinetic coefficients corresponding to cross effects. It is necessary to show that

$$D_{kk'}(r,r',t_1) = D_{k'k}(r,r',t_1), \qquad D_k^T(r,r',t_1) = \bar{D}_k^T(r,r',t_1). \tag{15}$$

Since the autocorrelation parts of these correlators are equal owing to microscopic reversibility, it is necessary only to establish the equalities

$$n_k(r',t+t_1)\langle \hat{J}_{k'\alpha}(r)\hat{P}_\alpha(r',t_1)\rangle_l = n_{k'}(r',t+t_1)\langle \hat{J}_{k\alpha}(r)\hat{P}_\alpha(r',t_1)\rangle_l; \tag{16a}$$

$$n_k(r',t+t_1)\langle \hat{Q}_\alpha(r)\hat{P}_\alpha(r',t_1)\rangle_l = h(r',t+t_1)\langle \hat{J}_{k\alpha}(r)\hat{P}_\alpha(r',t_1)\rangle_l. \tag{16b}$$

For this purpose we shall show that they are satisfied for $t_1 = 0$, and then show that, for $t_1 = 0$, equality holds between the derivatives of their left- and right-hand sides. To simplify the calculations we shall use the locally equilibrium canonical ensemble. As a result of simple calculations we obtain

$$n_k(r',t)\langle \hat{J}_{k'\alpha}(r)\hat{P}_\alpha(r')\rangle_l = 3n_k(r,t)n_{k'}(r,t)\beta^{-1}(r,t)\delta(r-r'); \tag{17}$$

$$\begin{aligned} n_k(r',t)\langle \hat{Q}_\alpha(r)\hat{P}_\alpha(r')\rangle_l = \delta(r-r')\, n_k(r,t)\beta^{-1}(r,t)\times \\ \times \sum_{k'=1}^{L} n_{k'}(r,t)\left\{\frac{15}{2}\beta^{-1}(r,t) + \frac{3}{2}\sum_{k_1=1}^{L} n_{k_1}(r,t)\int dr_1\left[\Phi^{(k'k_1)}(r_1) - \right.\right. \\ \left.\left. -\frac{r_1}{3}\frac{d\Phi^{(k'k_1)}(r_1)}{dr_1}\right] g_2^{(k'k_1)}(r_1)\right\}, \end{aligned} \tag{18}$$

where the locally equilibrium "radial" distribution function is

$$g_2^{(k'k_1)}(r_1-r_2) = \int dp_1 dp_2 N_{k_1}(N_{k'} - \delta_{k'k_1}) \frac{\overline{\rho_l(x_1^{(1)},\dots,x_{N_1}^{(I)},x_1^{(2)},\dots,x_{N_L}^{(L)})}}{x_1^{(k')} = x_1,\ x_{1+\delta_{k'k_1}}^{(k_1)} = x_2},$$

and the bar over ρ_l denotes integration over the variables of all particles except the first particle of species k' and the $(1+\delta_{k'k_1})$-th particle of species k_1.

On the other hand, according to (17),

$$h(r',t)\langle\hat{J}_{k\alpha}(r)\hat{P}_\alpha(r')\rangle_l = 3n_k(r,t)h(r,t)\beta^{-1}(r,t)\delta(r-r'), \tag{19}$$

and by the definition of the enthalpy $h = E + p$,

$$h(r,t) = \sum_{k=1}^{L} n_k(r,t)\left\{\frac{5}{2}\beta^{-1}(r,t) + \right. \\ \left. +\frac{1}{2}\sum_{k_1=1}^{L} n_{k_1}(r,t)\int dr_1\left[\Phi^{(kk_1)}(r_1) - \frac{r_1}{3}\frac{d\Phi^{(kk_1)}(r_1)}{dr_1}\right] g_2^{(kk_1)}(r_1)\right\}. \tag{20}$$

It follows from relations (17)–(20) that relations (16) are satisfied for $t_1 = 0$. Moreover, the derivatives of the correlators in formulas (16) with respect to t_1 at $t_1 = 0$ vanish. Thus, relations (16) are satisfied, and, consequently, the generalized symmetry relations are established.

It is now easy to show that relations (12) are satisfied. Indeed,

$$\begin{aligned}\langle\hat{P}_\alpha(r)\hat{I}_{k\alpha}(r',t_1)\rangle_l &= \langle\hat{P}_\alpha(r)\hat{J}_{k\alpha}(r',t_1)\rangle_l - \frac{n_k}{\rho}\sum_{k'=1}^{L} m_{k'}\langle\hat{J}_{k'\alpha}(r)\hat{P}_\alpha(r',t_1)\rangle_l \\ &= \langle\hat{P}_\alpha(r)\hat{J}_{k\alpha}(r',t_1)\rangle_l - \langle\hat{J}_{k\alpha}(r)\hat{P}_\alpha(r',t_1)\rangle_l = 0;\end{aligned} \tag{21}$$

$$\begin{aligned}\langle\hat{P}_\alpha(r)\hat{S}_\alpha(r',t_1)\rangle_l &= \langle\hat{P}_\alpha(r)\hat{Q}_\alpha(r',t_1)\rangle_l - \frac{h}{\rho}\sum_{k=1}^{L} m_k\langle\hat{J}_{k\alpha}(r)\hat{P}_\alpha(r',t_1)\rangle_l \\ &= \langle\hat{P}_\alpha(r)\hat{Q}_\alpha(r',t_1)\rangle_l - \langle\hat{Q}_\alpha(r)\hat{P}_\alpha(r',t_1)\rangle_l = 0\end{aligned} \tag{22}$$

owing to microscopic reversibility.

The author expresses his gratitude to D. N. Zubarev for discussion of the questions touched upon in this work.

Received
18 IV 1968

REFERENCES

1. H. Mori, Phys. Rev., **112**, 1829 (1958).

2. J. A. McLennan, Adv. Chem. Phys., **5**, 261 (1963).

3. L. Kadanoff, P. C. Martin, Ann. Phys., **24**, 419 (1963).

4. D. N. Zubarev, DAN, **164**, 537 (1965).

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