# APPLICATION OF THE NONEQUILIBRIUM STATISTICAL OPERATOR IN THE THEORY OF ENERGY EXCHANGE BETWEEN TWO SUBSYSTEMS

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## Abstract

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# APPLICATION OF THE NONEQUILIBRIUM STATISTICAL OPERATOR IN THE THEORY OF ENERGY EXCHANGE BETWEEN TWO SUBSYSTEMS

*(Presented by Academician N. N. Bogolyubov on 22 I 1968)*

The method of the nonequilibrium statistical operator (n.s.o.) ([1,2]), like Kubo's linear-response theory, correctly describes nonequilibrium processes for small deviations from statistical equilibrium, i.e., in the linear approximation ([3,4]). It remains unclear how correctly it describes strongly nonequilibrium, nonlinear processes. In the present work, using the concrete example of energy exchange between two subsystems—two low-density gases with strongly different temperatures—it is shown that the n.s.o. method leads to results coinciding with the results of kinetic theory. The large temperature difference is ensured by the slowness of the energy exchange (for example, owing to a large difference in masses), which is the small parameter of the problem.

Let us write the Hamiltonian of a mixture of two gases as

$$H = H_1 + H_2 = T_1 + U + T_2, \qquad H_1 = T_1 + U,$$

$$T_1 = \sum_{\alpha} E_\alpha a_\alpha^+ a_\alpha, \qquad T_2 = \sum_{\mu} E_\mu b_\mu^+ b_\mu, \tag{1}$$

$$U = \sum_{\alpha\mu\alpha'\mu'} \langle \alpha\mu|\Phi|\alpha'\mu'\rangle a_\alpha^+ b_\mu^+ b_{\mu'} a_{\alpha'}, \tag{2}$$

where $\alpha, \mu$ are the quantum numbers for particles of the first and second species; $\Phi$ is the interaction potential of these particles. Bearing in mind the application of the theory to a dilute gas, we neglect the interaction of identical particles. We calculate the operators of the energy fluxes between the subsystems

$$J_1 = \dot{H}_1 = \frac{1}{i\hbar}[H_1, H] = -\dot{H}_2 = -J_2 =$$

$$= \frac{1}{i\hbar} \sum_{\alpha\mu\alpha'\mu'} (E_{\mu'} - E_{\mu}) \langle \alpha\mu|\Phi|\alpha'\mu'\rangle a^+_{\alpha} b^+_{\mu} b_{\mu'} a_{\alpha'}. \tag{3}$$

Following (1), we write the n.s.o. as a function of specially constructed integrals of motion

$$\rho = \frac{1}{Q} e^{-A-B}, \qquad Q = \mathrm{Sp}\, e^{-A-B}, \tag{4}$$

$$A = \beta_1(H_1 - \mu_1 N_1) + \beta_2(H_2 - \mu_2 N_2), \tag{5}$$

$$B = -\int_{-\infty}^{0} dt\, e^{\varepsilon t} (\beta_1 - \beta_2) J_1(t), \tag{6}$$

where $\beta_1, \beta_2$ are the inverse temperatures; $\mu_1, \mu_2$ are the chemical potentials; $N_1, N_2$ are the corresponding particle-number operators. Generally speaking, relaxation processes should be described by means of a nonstationary statistical operator. However, it can be shown that taking nonstationarity into account leads to terms of higher order of smallness in the expression for

of the mean energy flux; therefore we introduced a stationary NSO, assuming that the parameters can change slowly in time. In accordance with the assumption that the energy transfer is small, the flux (3), and consequently also $B$, will be regarded as small quantities. In the zeroth approximation we obtain a quasiequilibrium distribution with a temperature discontinuity

$$\rho_q = \frac{1}{Q_q} e^{-A}, \qquad Q_q = \mathrm{Sp}\, e^{-A}. \tag{7}$$

Let us average the flux (3) over the ensemble (4), restricting ourselves to terms of first order in $B$:

$$\langle J_1 \rangle = (\beta_1 - \beta_2) \int_{-\infty}^{0} dt\, e^{\varepsilon t} \int_0^1 d\lambda\, \langle J_1 e^{-\lambda A} J_1(t) e^{\lambda A} \rangle_q. \tag{8}$$

Here $\langle ... \rangle_q$ denotes averaging over the ensemble (7). Outwardly this relation looks like a linear Kubo relation between the flux and the thermodynamic force $(\beta_1 - \beta_2)$; however, the averaging is performed not over an equilibrium ensemble, but over the quasiequilibrium ensemble (7), whence follows the nonlinearity of the flux (8) with respect to $(\beta_1 - \beta_2)$. Relation (8) is valid not only for rarefied gases, but also for dense gases and liquids (it is only necessary in (1) to take into account the interaction between identical particles).

Substituting (3) into (8), we obtain

$$\langle J_1\rangle = -\int_{-\infty}^{0} dt\, e^{\varepsilon t}(\beta_1-\beta_2)\frac{1}{i\hbar}\times \\ \times \sum_{\alpha\mu\alpha'\mu'}\sum_{\alpha_1\mu_1\alpha_1'\mu_1'}(E_{\mu_1'}-E_{\mu_1})(E_{\mu'}-E_{\mu})\langle\alpha\mu|\Phi|\alpha'\mu'\rangle\langle\alpha_1\mu_1|\Phi|\alpha_1'\mu_1'\rangle, \tag{9}$$

$$G^{\alpha\mu\alpha'\mu'}_{\alpha_1'\mu_1'\alpha_1\mu_1}(-t)\left[\beta_1(E_\alpha-E_{\alpha'})+\beta_2(E_\mu-E_{\mu'})\right]^{-1},$$

where the Green' s function has been introduced,

$$G^{\alpha\mu\alpha'\mu'}_{\alpha_1'\mu_1'\alpha_1\mu_1}(t-t_1) = (i\hbar)^{-1}\theta(t-t_1)\times$$

$$\times\left\langle\left[a^+_\alpha b^+_\mu b_{\mu'}a_{\alpha'}, \exp\left(-\frac{iH(t-t_1)}{\hbar}\right)a^+_{\alpha_1}b^+_{\mu_1'}b_{\mu_1}a_{\alpha_1'}\exp\left(\frac{iH(t-t_1)}{\hbar}\right)\right]\right\rangle_q, \tag{10}$$

a generalization of the ordinary two-time retarded Green' s function ([5,6]) to the case of a quasiequilibrium ensemble. Differentiating (10) with respect to $t$, we obtain the equation for the Green' s function

$$i\hbar\frac{\partial}{\partial t}G^{\alpha\mu\alpha'\mu'}_{\alpha_1'\mu_1'\alpha_1\mu_1}(t) + \sum_{\alpha_2\mu_2}\Big[\langle\alpha'\mu_1'|H^{(2)}|\alpha_2\mu_2\rangle G^{\alpha\mu\alpha'\mu'}_{\alpha_2\mu_2\alpha_1\mu_1}(t) \\ -G^{\alpha\mu\alpha'\mu'}_{\alpha_1'\mu_1'\alpha_2\mu_2}(t)\langle\alpha_2\mu_2|H^{(2)}|\alpha_1\mu_1\rangle\Big] + F^{\alpha\mu\alpha'\mu'}_{\alpha_1'\mu_1'\alpha_1\mu_1}(t) \\ = \delta(t)\delta_{\alpha\alpha_1}\delta_{\mu\mu_1}\delta_{\alpha'\alpha_1'}\delta_{\mu'\mu_1'}K_{\alpha\mu\alpha'\mu'}. \tag{11}$$

Here $H^{(2)}$ is the two-particle Hamiltonian, and $F(t)$ is a term with Green' s functions of higher order, which we do not write out explicitly. In what follows, considering the limiting case of a rarefied gas, we shall omit the term $F(t)$ in (11), thereby closing the equation. Then

$$K_{\alpha\mu\alpha'\mu'} = i\hbar G^{\alpha\mu\alpha'\mu'}_{\alpha\mu\alpha'\mu'}(+0) = n_\alpha n_\mu(1\pm n_{\alpha'})(1\pm n_{\mu'}) - n_{\alpha'}n_{\mu'}(1\pm n_\alpha)(1\pm n_\mu), \tag{12}$$

where the plus sign is taken for Bose statistics and the minus sign for Fermi statistics; $n_\alpha, n_\mu$ are occupation numbers,

$$n_\alpha = \left(\exp[\beta_1(E_\alpha - \mu_1)] \mp 1\right)^{-1}, \qquad n_\mu = \left(\exp[\beta_2(E_\mu - \mu_2)] \mp 1\right)^{-1}. \quad (13)$$

The solution of equation (11) has the form

$$G^{\alpha\mu\alpha'\mu'}_{\alpha_1'\mu_1'\alpha_1\mu_1} = \frac{1}{i\hbar}\theta(t)\left\langle \alpha'\mu' \left| \exp\left(-\frac{i}{\hbar}H^{(2)}t\right) \right| \alpha_1\mu_1 \right\rangle \times$$
$$\times \left\langle \alpha_1'\mu_1' \left| \exp\left(\frac{i}{\hbar}H^{(2)}t\right) \right| \alpha\mu \right\rangle K_{\alpha\mu\alpha'\mu'}. \quad (14)$$

Substituting (14) into (10), we obtain

$$\langle J_1\rangle = -\int_\infty dt\, e^{\varepsilon t}(\beta_1 - \beta_2)\frac{1}{(i\hbar)^2}\sum_{\alpha\mu\alpha'\mu'}\sum_{\alpha_1\mu_1\alpha_1'\mu_1'}\left\langle \alpha\mu \left| \Phi \exp\left(\frac{i}{\hbar}H^{(2)}t\right) \right| \alpha'\mu' \right\rangle \times$$
$$\times \left\langle \alpha'\mu' \left| (h_2(-t) - E_\mu) f_{\alpha\mu}(h_1(-t), h_2(-t)) \right| \alpha_1\mu_1 \right\rangle \times$$
$$\times \left\langle \alpha_1\mu_1 \left| \Phi \exp\left(-\frac{i}{\hbar}H^{(2)}t\right) \right| \alpha_1'\mu_1' \right\rangle \left\langle \alpha_1'\mu_1' \left| h_2(t) - E_{\mu_1} \right| \alpha\mu \right\rangle, \quad (15)$$

where $h_1$ and $h_2$ are the single-particle Hamiltonians of the particles of the first and second sorts; $H^{(2)} = h_1 + h_2 + \Phi$; furthermore,

$$f_{\alpha\mu}(E_{\alpha'}, E_{\mu'}) = K_{\alpha\mu\alpha'\mu'}\left[\beta_1(E_\alpha - E_{\alpha'}) + \beta_2(E_\mu - E_{\mu'})\right]^{-1}; \quad (16)$$

the time argument of $h_1$ and $h_2$ in (15) denotes the Heisenberg representation. It is not difficult to notice that in the matrix elements

$$\left\langle \alpha'\mu' \left| (h_2(-t) - E_\mu) f_{\alpha\mu}(h_1(-t), h_2(-t)) \right| \alpha_1\mu_1 \right\rangle,$$

$$\left\langle \alpha_1'\mu_1' \left| (h_2(t) - E_{\mu_1}) \right| \alpha\mu \right\rangle$$

one may omit the dependence on $t$, which is equivalent to neglecting terms of order $v^3t^3/V$, where $v$ is the relative velocity of the colliding particles, $V$ is the volume of the system. For finite $\varepsilon$ in (15), the integrand differs noticeably from zero only at times of order $\varepsilon^{-1}$; therefore $v^3t^3/V \sim v^3/V\varepsilon^3$, whence it follows that, with the correct order of limiting transitions—first $V \to \infty$, and then $\varepsilon \to 0$ —the discarded terms vanish. It is essential that, in this way, waves reflected from the boundaries of the volume are automatically excluded.

As follows from the formal scattering theory (7), for $|t| \gg \tau_c$, where $\tau_c$ is the collision time, one may put

$$\left\langle \alpha\mu \middle| \Phi \exp\left(\pm\frac{i}{\hbar}H^{(2)}t\right) \middle| \alpha'\mu' \right\rangle = e^{\pm\frac{i}{\hbar}(E_{\alpha'}+E_{\mu'})t} \begin{cases} \langle \alpha\mu \left| T \right| \alpha'\mu' \rangle, & \text{for } +, \\ \langle \alpha\mu \left| T^{+} \right| \alpha'\mu' \rangle, & \text{for } -, \end{cases} \quad (17)$$

where $\langle \alpha\mu | T | \alpha'\mu' \rangle$ are the matrix elements of the scattering $T$-matrix. Neglecting in (15) times of the order of the collision time, we obtain

$$\langle J_1 \rangle = \frac{2\pi}{\hbar} \sum_{\alpha\mu\alpha'\mu'} \left| \langle \alpha\mu \left| T \right| \alpha'\mu' \rangle \right|^2 E_\alpha \left[ n_\alpha n_\mu (1 \pm n_{\alpha'})(1 \pm n_{\mu'}) - \right.$$

$$\left. - n_{\alpha'} n_{\mu'} (1 \pm n_\alpha)(1 \pm n_\mu) \right] \delta(E_\alpha + E_\mu - E_{\alpha'} - E_{\mu'}).$$

Thus, starting from the nonequilibrium statistical operator (4), for the mean energy flux a nonlinear expression (8) in the thermodynamic forces has been obtained, which in the limit of low densities agrees with kinetic theory.

The technique developed here is easily transferred to the case of relaxation of internal degrees of freedom and to simple homogeneous chemical reactions.

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