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Abstract

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Transport Processes in Systems Connected by a Capillary

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Let us consider the process of transport of energy and particles between two systems connected by a capillary or a membrane, using the method set forth in work (^{1}). Each of the systems is in thermal and material contact with its own thermostat, so that temperatures T_1 and T_2 and chemical potentials μ_1 and μ_2 are established in them. The capillary (or membrane), whose nature is not essential for what follows, makes possible an exchange of energy and particles between the systems. This problem was considered, with the aid of Onsager' s theory in the thermodynamics of irreversible processes, by B. Deryagin and G. Sidorenkov (^{2}), and later by de Groot (^{3}).

The total Hamiltonian H and the particle-number operator N are equal to $H = H_1 + H_2$, $N = N_1 + N_2$, where H_i and N_i are, respectively, the Hamiltonian and the particle-number operator of system i. The interaction of the systems may be neglected, since they are spatially separated.

The total Hamiltonian and the number of particles are integrals of motion, i.e. $\dot{H} = \dot{H}_1 + \dot{H}_2$, $\dot{N} = \dot{N}_1 + \dot{N}_2$. Here a dot denotes the time derivative of an operator at $t = 0$, for example: $\dot{H}_i = \frac{1}{i\hbar}[H_i, H]$. In the case of classical statistical mechanics one must replace the quantum Poisson brackets by classical ones. We introduce the operators of the energy and particle-number currents $J_H = \dot{H}_1$, $J_N = \dot{N}_1$, describing the rate of exchange of energy and particles between the systems. The conservation laws may be written in the Heisenberg representation:

$$\begin{aligned} \dot{H}_1(t) - J_H(t) &= 0, & \dot{N}_1(t) - J_N(t) &= 0, \\ \dot{H}_2(t) + J_H(t) &= 0, & \dot{N}_2(t) + J_N(t) &= 0. \end{aligned} \tag{1}$$

Explicit expressions for the operators J_H and J_N are obtained from the conservation laws for energy and number of particles in operator form: $\dot{H}(x) + \operatorname{div} \mathbf{j}_H(x) = 0$, $\dot{n}(x) + \operatorname{div} \mathbf{j}(x) = 0$. Integrating these relations over the volume of the first system, we obtain expressions for $\dot{H}_1$, $\dot{N}_1$, J_H, J_N:

$$\dot{H}_1 = \int_{V_1} \dot{H}(x)\,dx, \qquad \dot{N}_1 = \int_{V_1} \dot{n}(x)\,dx,$$

$$J_H = -\int_{S_1} (\mathbf{j}_H(x)\,d\mathbf{s}) = \int_{S_2} (\mathbf{j}_H(x)\,d\mathbf{s}), \qquad J_N = -\int_{S_1} (\mathbf{j}(x)\,d\mathbf{s}) = \int_{S_2} (\mathbf{j}(x)\,d\mathbf{s}), \tag{2}$$

where V_1 and S_1 are the volume and surface of the first system. The integration over the surface of the system is, of course, reduced to integration over that part of the system surface where the membrane connecting the systems is located; in the case of a capillary, a certain part of the surface near it, in addition to the capillary aperture, may be significant.

On the basis of the conservation laws (1), one can construct 4 integrals of motion A_1, A_2, B_1, B_2:

$$\begin{aligned} A_1 &= H_1 - \int_{-\infty}^{0} J_H(t)\,dt, \qquad & A_2 &= H_2 + \int_{-\infty}^{0} J_H(t)\,dt, \\ B_1 &= N_1 - \int_{-\infty}^{0} J_N(t)\,dt, \qquad & B_2 &= N_2 + \int_{-\infty}^{0} J_N(t)\,dt \end{aligned} \tag{3}$$

with the boundary conditions of absence of fluxes at $t = -\infty$: $J_H(-\infty) = J_N(-\infty) = 0$. These conditions may be replaced by the condition of the existence of the integrals $\lim_{\varepsilon\to 0} \int_{-\infty}^{0} e^{\varepsilon t} J_H(t)\,dt$, $\lim_{\varepsilon\to 0} \int_{-\infty}^{0} e^{\varepsilon t} J_N(t)\,dt$, if the integrals in (3) are considered in the sense of the limiting transition $\varepsilon \to 0$ (first $V \to \infty$).

If the statistical operator is chosen in the form of a function of the operators A_i, B_i, then it will also be an integral of motion. We choose the statistical operator ρ in the form

$$\rho = Q^{-1} \exp\left\{ -\sum_i \beta_i (A_i - \mu_i B_i) \right\}, \tag{4}$$

where Q is the normalizing factor, $\beta_i = 1/T_i$; μ_i are parameters having the meaning of the inverse temperature and chemical potential of system i.

It is convenient to introduce the thermodynamic forces

$$X_H = \Delta\beta = \beta_1 - \beta_2,$$
$$X_N = -\Delta\beta\mu = \beta_2\mu_2 - \beta_1\mu_1;$$

then

$$\rho = Q^{-1} \exp\left\{ -\sum_i \beta_i (H_i - \mu_{iN} i) + \int_{-\infty}^{0} (J_H(t) X_H + J_N(t) X_N)\, dt \right\} \tag{5}$$

or

$$\rho = Q^{-1} \exp\left\{ -\sum_i \left\{ \beta_i (H_i - \mu_{iN} i) - \int_{-\infty}^{0} J_i(t) X_i \, dt \right\} \right\}, \tag{5a}$$

where $X_1 = X_H,\ X_2 = X_N,\ J_1 = J_H,\ J_2 = J_N$.

For $\beta_1 = \beta_2 = \beta,\ \mu_1 = \mu_2 = \mu$, (5) goes over into the Gibbs distribution for the grand ensemble $\rho = Q^{-1} e^{-\beta(H-\mu N)}$.

In the case where the differences of temperatures and chemical potentials are small, ρ can be expanded in a series in the thermodynamic forces and one may restrict oneself to linear terms. To this end write ρ in the form $\rho = Q^{-1} e^{-A-B}$, where

$$A = \sum_i \beta_i (H_i - \mu_{iN} i), \qquad B = -\sum_i \int_{-\infty}^{0} J_i(t) X_i \, dt.$$

To accuracy up to terms linear in B, we obtain

$$\rho = \rho_0 \left\{ 1 - \int_0^1 \left(e^{A\tau} B e^{-A\tau} - \left\langle e^{A\tau} B e^{-A\tau} \right\rangle \right) d\tau \right\}, \tag{6}$$

where $\rho_0 = e^{-A} / \operatorname{Sp} e^{-A}$, $\langle ... \rangle = \operatorname{Sp}(\rho_0 \, ...)$.

With the aid of (6) we find

$$\overline{J}_k = \operatorname{Sp}(\rho J_k) = \sum_k \int_0^{\beta} \int_{-\infty}^{0} \langle J_{kJ} m(t + i\hbar\tau) \rangle \, X_m \, d\tau \, dt, \tag{7}$$

where we have used the condition $\langle J_k \rangle = 0$, since $\langle \dot{J}_k \rangle = 0$ (the averaging is carried out over the equilibrium Gibbs ensemble).

We write relation (7) in the standard form adopted in Onsager theory:

$$\overline{J}_k = \sum_m L_{km} X_m, \tag{8}$$

where

$$L_{km} = \int_0^{\beta} \int_{-\infty}^{0} \langle J_k J_m(t + i\hbar\tau) \rangle \, d\tau \, dt \tag{9}$$

are kinetic coefficients. They can also be expressed through two-time retarded Green' s functions,

$$L_{km} = \int_{-\infty}^{0} \int_{-\infty}^{t} \langle\langle J_m(t') J_k \rangle\rangle \, dt \, dt', \tag{10}$$

where

$$\langle\langle J_m(t) J_k \rangle\rangle = \frac{1}{i\hbar} \langle [J_m(t), J_k] \rangle$$

for $t < 0$, and is equal to zero for $t > 0$.

The kinetic coefficients can be written, using (2), in a more explicit form

$$L_{km} = \iint_{S_1} \langle \mathbf{n} \cdot \mathbf{j}_k(x) \, \mathbf{n}' \cdot \mathbf{j}_m(x', t + i\hbar\tau) \rangle \, ds \, ds' \, d\tau \, dt, \tag{11}$$

where $\mathbf{n}, \mathbf{n}'$ are the normals to the membrane surface or, in the case of a capillary, the normals to the surface bounding the capillary opening and to the vessel surface lying near it.

Formula (11) establishes the relation between volume and surface kinetic coefficients. Indeed, if one introduces the tensor, defined in the volume of the system,

$$L_{km}(x, x') = \int_0^{\beta} \int_{-\infty}^{0} \langle \mathbf{j}_k(x) \mathbf{j}_m(x', t + i\hbar\tau) \rangle \, d\tau \, dt, \tag{12}$$

already considered in the theory of transport processes (4,1), then the kinetic coefficients (11) can be calculated from the formula

$$L_{km} = \iint_{S_1} \mathbf{n} \cdot L_{km}(x, x') \cdot \mathbf{n}' \, ds \, ds'. \tag{13}$$

The integrand in (13) is the complete contraction of the tensor with the normal vectors $\mathbf{n}$ and $\mathbf{n}'$.

For an actual calculation of the quantities L_{km}, it is, of course, necessary to know the correlation function $L_{km}(x, x')$, and for this one must solve the boundary-value problem for the Green' s function with boundary conditions specified on the surface of the membrane or capillary. Such a problem has not yet been considered.

The symmetry property of the coefficients L_{km} in the absence of a magnetic field (Onsager' s theorem), $L_{km} = L_{mk}$, follows from the symmetry of the coefficients $L_{km}(x, x')$. With the aid of relations (8),

$$J_H = L_{11} X_H + L_{12} X_N, \qquad J_N = L_{21} X_H + L_{22} X_N \tag{14}$$

one can study the thermomolecular pressure difference. For this it is convenient to pass to the variables pressure and temperature and to introduce the thermodynamic potential $\Phi(p, T) = N\mu$. Then

$$\Delta\mu = \frac{1}{N}\left\{\frac{\partial\Phi}{\partial p}\Delta p + \frac{\partial\Phi}{\partial T}\Delta T\right\} = v\Delta p - s\Delta T, \tag{15}$$

where $v = V/N,\ s = S/N$ are, respectively, the specific volume and entropy.

The thermodynamic forces are equal to

$$X_N = -\frac{\Delta\mu}{T} + \frac{\mu\Delta T}{T^2} = -\frac{v}{T}\Delta p + \frac{h}{T^2}\Delta T, \qquad X_H = -\frac{\Delta T}{T^2}, \tag{16}$$

where $h = \mu + sT$ is the specific enthalpy.

Substituting (16) and (14), we obtain the well-known relations

$$J_H = -\frac{L_{12} v}{T}\Delta p + \frac{L_{12} h - L_{11}}{T^2}\Delta T,$$

$$J_N = -\frac{L_{22} v}{T}\Delta p + \frac{L_{22} h - L_{21}}{T^2}\Delta T, \tag{17}$$

but now with completely definite values of L_{ik}. If the process is isothermal ($\Delta T = 0$), then, owing to the pressure difference, a thermomechanical effect arises, i.e., an energy flux equal to

$$J_H = U^* J_N, \tag{18}$$

where the quantity

$$U^* = \frac{L_{12}}{L_{22}} = \frac{\int_0^\beta \int_{-\infty}^0 \langle J_H J_N(t + i\hbar\tau)\rangle \, d\tau \, dt}{\int_0^\beta \int_{-\infty}^0 \langle J_N J_N(t + i\hbar\tau)\rangle \, d\tau \, dt} \tag{19}$$

is called the energy of transfer. Thus we have obtained an expression for the energy of transfer through correlation functions. The energy of transfer can be represented in another, more explicit form

$$U^* = \frac{\int_{S_1}\int\int_0^\beta\int_{-\infty}^0 \mathbf{n}\cdot\langle\mathbf{j}_H(x)\mathbf{j}(x',t+i\hbar\tau)\rangle\cdot\mathbf{n}'\,ds\,ds'\,d\tau\,dt}{\int_{S_2}\int\int_0^\beta\int_{-\infty}^0 \mathbf{n}\cdot\langle\mathbf{j}(x)\mathbf{j}(x',t+i\hbar\tau)\rangle\cdot\mathbf{n}'\,ds\,ds'\,d\tau\,dt} \tag{20}$$

or through two-time Green functions

$$U^* = \frac{\int_{S_1}\int\int_{-\infty}^0\int_{-\infty}^t \mathbf{n}'\cdot\langle\!\langle\mathbf{j}(x',t)\mathbf{j}_H(x)\rangle\!\rangle\cdot\mathbf{n}\,ds\,ds'\,dt\,dt'}{\int_{S_1}\int\int_{-\infty}^0\int_{-\infty}^t \mathbf{n}'\cdot\langle\!\langle\mathbf{j}(x',t)\mathbf{j}(x)\rangle\!\rangle\cdot\mathbf{n}'\,ds\,ds'\,dt\,dt}. \tag{21}$$

If the energy flux is equal to zero, then a difference of thermomolecular pressures is established (2,3)

$$\frac{\Delta p}{\Delta T} = \frac{h - L_{21}/L_{22}}{vT} = \frac{h - U^*}{vT},$$

which can be found by means of (20), (21).

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