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SYMMETRY PROPERTIES OF THE DIFFUSION TENSOR IN THE THEORY OF NEW PHASE FORMATION

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The classical theory of the growth of a new phase with phase transitions of the first kind [1-5] is based on a consideration of the diffusion of the new phase seed in the space of their dimension through a potential barrier which occurs because of the competition between the volume and surface energies. In a number of cases, it turns out to be necessary to characterize the seed by two or more variables rather than one. Thus, in the most popular problem of mixture condensation, the natural variables are the numbers of molecules of the mixture components in the seed, and in different problems of the theory of cavitation it is expedient to use the density [6] or rate of growth [7] of the seed as variables in addition to the dimension, finally, the seed temperature [8] plays the part of an additional parameter in taking account of the incomplete thermal equilibrium between the seed and the medium.

The evolution of a nonequilibrium distribution function $f(\mathbf{x}, t)$ of the seed-characterizing parameters $\mathbf{x} = \{x_i\}$ is determined by the multidimensional Fokker–Planck equation

$$I_i = \varphi(\mathbf{x}) \sum_j D_{ij}(\mathbf{x}) \frac{\partial}{\partial x_j}\left(\frac{f(\mathbf{x}, t)}{\varphi(\mathbf{x})}\right), \quad \frac{\partial f}{\partial t} + \sum_i \frac{\partial I_i}{\partial x_i} = 0, \tag{1}$$

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where $\varphi \sim \exp(-U(\mathbf{x})/kT)$ is a quasiequilibrium distribution function describing the fluctuation seed distribution, $U(x)$ is the minimal work in forming a seed with the parameters $\mathbf{x}$, T is the temperature, and (1) is valid if the characteristic scales x_i and t are large compared to the jumps Δx_i (generally discrete) in the variables x_i and with relaxation time τ of the remaining variables of the system to the incomplete equilibrium characterized by giving $\mathbf{x}$.

In considering the problem in a stationary formulation when supersaturation is kept constant, and the growing seeds are removed, the point $\mathbf{x}_c$ of the crossing $U(\mathbf{x})$ plays a fundamental part in the calculation of the growth rate and the other new phase characteristics (completely analogously to the maximum point U in one-dimensional theory), only values of $D_{ij}(\mathbf{x}_c)$ [6, 9] enter into the final expression (on which the composition, temperature, etc. of the growing seeds generally depend strongly). It can be seen that the macroscopic equations of motion $\dot{x}_i = \dot{x}_i(\mathbf{x})$ combined with (1) for an individual seed have the form as $\mathbf{x} \to \mathbf{x}_c$

$$\dot{x}_i = -\sum_j D_{ij} X_j, \; X_j = \frac{\partial U}{\partial x_j}, \tag{2}$$

which agrees formally with the form of the kinetic equations in the neighborhood of the ordinary equilibrium point corresponding to the minimum $U(x)$. It is well known that the principle of microscopic reversibility of the time results, in the latter case, in the Onsager symmetry relationships

$$D_{ij}(\mathbf{x}_{\min}) = D_{ji}(\mathbf{x}_{\min}). \tag{3}$$

Expressions for $\mathbf{D}$ satisfying the relationships

$$D_{ij}(\mathbf{x}_c) = D_{ji}(\mathbf{x}_c), \tag{4}$$

which are formally analogous to (3), have been obtained in a number of papers on the theory of mixture condensation [9, 10] and nonisothermal condensation [8], where compliance with (4) is related to the Onsager principle in certain researches [8].

In this paper we obtain an expression for $\mathbf{D}$ in the problem of binary mixture condensation, and we show that satisfying (4) is related to the model nature of the approximations used in [6, 9, 10, 11].

First of all, let us note that compliance with (4) has no relation to the principle of microscopic reversibility. In fact, the values of $D_{ij}(\mathbf{x}_c)$ plays a role only in a strongly nonequilibrium state with stationary seed flux when the point $\mathbf{x}_c$ is isolated. But the principle of microscopic reversibility is known not to hold in this state, for the substitution $t \to -t$ the direction of the seed flux changes. A more formal derivation can be performed. To do this, we go over to the variables $\mathbf{y} = \{y_i\}$ in which

$$\frac{U(\mathbf{x})}{kT} = \frac{U(\mathbf{x}_c)}{kT} - \frac{A_0}{2} y_0^2 + \frac{1}{2} \sum_{i>0} A_i y_i^2, \quad A_i > 0, \quad i = 0,1\ldots$$

The equations of motion for the correlation functions $\langle y_i(t_1) y_j(t_2)\rangle$, follows from (2), where $\langle\ \rangle$ is averaging with respect to the Gibbs distribution

$$\frac{\partial}{\partial t_1} \langle y_i(t_1)\, y_k(t_2)\rangle = -\sum_j D_{ij} A_j \langle y_j(t_1)\, y_k(t_2)\rangle \tag{5}$$

(here D_{ij} is the diffusion tensor in the space $\langle y_i\rangle$).

Let us find the constraints imposed on $\mathbf{D}$ by the principle of microscopic reversibility. Proceeding analogously to the derivation of the usual Onsager relationships, we differentiate the reversibility condition $\langle y_i(t_1) y_k(t_2)\rangle = \langle y_i(t_2) y_k(t_1)\rangle$ with respect to t_1, and setting $t_1 = t_2$ we obtain $D_{ik} A_k \langle y_k^2\rangle = D_{ki} A_i \langle y_i^2\rangle$. For $i, k > 0$ $\langle y_i^2\rangle = A_i^{-1}$ from which the relationships (4) follow. The case $i = 0$ requires special investigation since $\langle y_0^2\rangle = \dfrac{\int \exp \frac{A_0}{2} y_0^2 y_0^2 dy_0}{\int \exp \frac{A_0}{2} y_0^2 dy_0}$ diverges, where the linear approximation (5) is known to be inapplicable in the domain $|y_0| \gg A_0^{-1/2}$ defining the integral. Therefore, within the framework of our analysis, the microscopic reversibility principle does not result in any constraints on the form of the coefficients D_{0k}, D_{k0}. Moreover, in going from $\{y_i\}$ to another set of variables by a linear approximation including y_0, the symmetry properties of the tensor D_{ik} ($i, k > 0$) generally vanish.

The symmetry relations (4) or other relations between the components of $\mathbf{D}$ can however be the result of continuing the kinetic equations (2) from the stability domain in the consideration of a specific model to which we turn.

Let us investigate the formation of the liquid phase seed in a weakly supersaturated gas mixture of the two components A and B. Let us examine the problem in a stationary formulation by considering that:

a) The grown seeds with volume V greater than a certain fixed volume V_1 are removed from the system; here it is understood $V_c \ll V_1 \ll V_0$, where V_c and V_0 are, respectively, the volumes of the critical seed and of the whole system;

b) Intense thermodynamic gas phase parameters are maintained during nucleation (for instance, the temperature T_0, and the chemical potentials μ_A^0 and μ_B^0).

The minimum work in the formation of seeds with energy E, entropy S, volume V, and numbers of molecules N_A and N_B can be written in standard form under conditions b) [11]

$$U = \Delta\left(E - T_0 S + p_0 V - \mu_A^0 N_A - \mu_B^0 N_B\right). \tag{6}$$

The temperature T of the seed can be considered to equal T_0 for not too high supersaturations (corresponding estimates are made in [12]). We then obtain from (6)

$$U = F_e + p_0 V - \mu_A^0 N_A - \mu_B^0 N_B, \tag{7}$$

where F_e is the seedfree energy. Considering surface-inactive substances for which the surface tension coefficient α is independent of the mixture concentration to simplify the formulas we use the representation $F_e = F_V + \alpha\sigma$, where σ is the seed surface area.* Under the assumption of incompressibility of the fluid, the equation of state does not contain p, i.e., has the form $V = V(N_A, N_B, T)$, which permits describing the seed by giving the numbers N_A and N_B. For thermodynamic forces conjugate to N_A and N_B, we obtain

$$\begin{aligned} X_A &= -\left(\frac{\partial U}{\partial N_A}\right)_{N_B, T} = \mu_A - \mu_A^0 - v_A (p - p_0), \\ X_B &= -\left(\frac{\partial U}{\partial N_B}\right)_{N_A, T} = \mu_B - \mu_B^0 - v_B (p - p_0), \end{aligned} \tag{8}$$

where μ_A, μ_B are the chemical potentials of the fluid

$$p = -\left(\frac{\partial F_e}{\partial V}\right)_{N_A, N_B, T} = -\left(\frac{\partial F_V}{\partial V}\right)_{N_A, N_B, T} - \frac{2\alpha}{r}$$

is the pressure taking account of the surface part, r is the seed radius, and v_A and v_B are the molecular volumes of the components in the liquid phase.

To evaluate the diffusion tensor $\mathbf{D}$, relating the fluxes $j_A = \dot{N}_A$ and $j_B = \dot{N}_B$ to the thermodynamic forces X_A, X_B by the relations

$$\mathbf{j} = \mathbf{D}\mathbf{X}, \tag{9}$$

where $\mathbf{j} = \{j_A, j_B\}$, $\mathbf{X} = \{X_A, X_B\}$ for brevity, specific assumptions must be made about the properties of the gas phase. It was assumed in [9, 10] that the gas phase is a mixture of ideal gases of molecules A, B and different molecular complexes AA, AB, BB, etc., where the acts of evaporation and condensation of each "component" including the complexes are independent, and their probabilities satisfy the detailed balance principle. As is shown in [10], the symmetry relationships (4) follow from these assumptions. Let us show that the correlation between elementary processes inevitably results in spoilage of (4).

Let us start with the simplest case

$$v_A^{1/3} \gg n_A \gg \max(n_{AA}, n_{AB} \ldots),\ v_B^{1/3} \gg n_B \gg \max(n_{BB}, n_{AB} \ldots),$$

where n is the volume density when the gas phase can be considered as a mixture of ideal gases A and B. Then the flows j_+ of the components from the gas phase in the seed are given by the usual gaskinetic formulas

$$\mathbf{j}_+ = \sigma\boldsymbol{\beta}\mathbf{n}, \tag{10}$$

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*In the general case, the surface term has the form $\alpha\sigma$ only for a high potential Ω_e.

where

$$\boldsymbol{\beta} = \left(\frac{kT}{2\pi}\right)^{1/2} \begin{pmatrix} m_A^{-1/2} & 0 \\ 0 & m_B^{-1/2} \end{pmatrix},$$

and m_A, m_B are the molecule masses.

Let us write the most general expression for $\mathbf{j}$ by taking account of the correlation between different elementary processes

$$\mathbf{j} = \mathbf{j}_0(N_A,\ N_B) + (1 - \mathbf{R}(c))\mathbf{j}_+,$$

where the diagonal elements of the matrix $\mathbf{R}$ are reflection coefficients of the molecules, and the nondiagonal elements describe the correlation between the molecule condensations of one component and the molecule evaporation of the other, and $c = N_B/N_A$ is the mixture concentration in the seed.

The difference R from zero is related mainly to the local heating of the fluid under consideration of the molecules, hence, all the components of R, are of generally the same order, where there is no foundation to consider them small compared to one. Moreover, in the case of nonisothermal condensation (i.e., for sufficiently small critical seeds in the absence of a gas carrier) there follows from the results in [12]

$$R_{AB} + R_{BB} \simeq R_{BA} + R_{AA} \simeq 1.$$

Let us consider a small change in supersaturation characterized by the variations $\delta\mu_A^0$, $\delta\mu_B^0$. Since $\mathbf{j}_0$ does not vary here, then

$$\delta\mathbf{j} = (1 - \mathbf{R})\delta\mathbf{j}_+ = (1 - \mathbf{R})\boldsymbol{\beta}\delta\mathbf{n}. \tag{11}$$

On the other hand, from (8)

$$\delta\mathbf{n} = \mathbf{C}\delta\mathbf{X}, \tag{12}$$

where in zeroth order in the gas parameters

$$C_{AA} = -\frac{n_A}{kT},\ C_{BB} = -\frac{n_B}{kT},\ C_{AB} = C_{BA} = 0.$$

From (11) and (12) we obtain $\delta\mathbf{j} = (1 - \mathbf{R})\boldsymbol{\beta}\mathbf{C}\delta\mathbf{X}$, or by comparison with (9), $\mathbf{D} = (1 - \mathbf{R})\boldsymbol{\beta}\mathbf{C}$. Thus

$$\frac{D_{AB}}{D_{BA}} = \left(\frac{m_A}{m_B}\right)^{1/2} \frac{n_B}{n_A} \frac{R_{AB}(c)}{R_{BA}(c)}. \tag{13}$$

On the phase equilibrium line

$$c_0 = \overline{c}_0(c,\ T),\ p_0 = \overline{p}_0(c,\ T), \tag{14}$$

where $c_0 = n_B/n_A$, (3) should be satisfied, which yields

$$D_{AB} = \frac{c_0}{\overline{c}_0} D_{BA}. \tag{15}$$

Defining c_0 at the labile equilibrium point from the Thomson formula for a mixture [13]

$$\mu_A(c) - \mu_A^0 = 2\frac{v_A\alpha}{r},\quad \mu_B(c) - \mu_B^0 = 2\frac{v_B\alpha}{r},$$

we find $c_0/\overline{c}_0 = \exp - 2v_B\alpha/r_0kT$ or in the case $cv_B \ll v_A$ of weak solutions

$$\frac{c_0}{\overline{c}_0} \simeq \exp - \left[2\left(\frac{3}{4\pi}\right)^{1/3} \frac{v_A^{2/3}\alpha}{kT} \frac{v_B}{v_A} N_A^{-1/3}\right].$$

Substituting the numerical values for the aqueous solution at T ~ 400°K, we find

$$\frac{c_0}{\overline{c}_0} \simeq \exp - \left[1.5 \frac{v_B}{v_A} N_A^{-1/3}\right]$$

and we see that (4) is spoiled in the case of macromolecular dissolved substances even for comparatively high critical seeds with $N_A \sim 10^2$-10^3. Because of the above relative to the components of R, the diagonal and nondiagonal elements of $\mathbf{D}$ hence generally have the same order of magnitude.

Let us extend the results obtained by taking account of the correlation in the gas phase. Let us start with the case when the presence of molecular complexes can be neglected*; it is known to be realized, say, for inert gases. Then, particle scattering which is quasiclassical because of the smallness $\hbar^2 n^{2/3}/mkT$ does not change the Maxwell distribution in the momenta, and (10) remains valid. Defining the relation between $\delta\mathbf{n}$ and $\delta\mathbf{X}$ from the expansions in the gas parameters

$$p_0 = kT\left[\xi_A + \xi_B - \frac{1}{2}\left(I_A\xi_A^2 + 2I_{AB}\xi_A\xi_B + I_B\xi_B^2\right) + \ldots\right],$$

$$n_A = \xi_A\,(1 - I_A\xi_A - 2I_{AB}\,\xi_B + \ldots),$$

$$n_B = \xi_B\,(1 - I_B\,\xi_B - 2I_{AB}\,\xi_A + \ldots),$$

where $\xi = (mkT/2\pi\hbar^2)^{3/2}\exp(\mu/kT)$ is the fugacity, and I are the second virtual coefficients, we find an expression for C in (12). To the accuracy of squares of the small parameters of the type $n_A v_A$, $I_A n_A$, etc., we obtain

$$C_{AA} = -\frac{n_A}{kT}(1 - I_A n_A + v_A n_A),$$

$$C_{BB} = -\frac{n_B}{kT}(1 - I_B n_B + v_B n_B), \quad C_{AB} = C_{BA} = -\frac{I_{AB} n_A n_B}{kT}.$$

Now we have in place of (13)

$$\frac{D_{AB}}{D_{BA}} = \frac{c_0 R_{AB}}{R_{BA}}\left(\frac{m_A}{m_B}\right)^{1/2}(1 + p_0\psi(c_0)),$$

$$\psi(c_0) = \frac{1}{kT(1+c_0)}\left(I_A - v_A - c_0(I_B - v_B) + \frac{I_{AB}(R_{AA}m_B - c_0 R_{BB} m_A)}{R_{AB} m_A^{1/2} m_B^{1/2}}\right),$$

from which we find by requiring satisfaction of (3) under the condition (14)

$$\frac{D_{AB}}{D_{BA}} = \frac{c_0}{\bar{c}_0}(1 + p\psi(c_0) - \bar{p}\psi(\bar{c}_0)).$$

Let us briefly write the results which result from taking account of the presence of complexes (AB for definiteness). For simplicity, we here neglect the effects considered above for the nonideality of the gas, and the sole difference from the approach in [9, 10] is taking account of the correlation between the elementary processes of evaporation and condensation. It can be verified that the minimal work of U retains the form (7) when taking account of the chemical equilibrium condition $\mu_A^\circ + \mu_B^\circ = \mu_{AB}^\circ$ relative to the formation of complexes. The flux of complexes on the seed surface from the gas is given by the formula

$$j_{AB}^{+} = \sigma\beta_{AB} n_{AB},$$

where $\beta_{AB} = (kT/2\pi(m_A + m_B))^{1/2}$, and n_{AB} is the concentration of the complexes. Trivially generalizing (11) and (12), we find

$$D_{AA} = \frac{\sigma}{kT}[(1 - R_{AA})\beta_A n_A + (1 - R_{AA} - R_{AB})\beta_{AB} n_{AB}],$$

$$D_{BB} = \frac{\sigma}{kT}[(1 - R_{BB})\beta_B n_B + (1 - R_{BB} - R_{BA})\beta_{AB} n_{AB}],$$

$$D_{AB} = \frac{\sigma}{kT}[(1 - R_{AA} - R_{AB})\beta_{AB} n_{AB} - \beta_B R_{AB} n_B],$$

$$D_{BA} = \frac{\sigma}{kT}[(1 - R_{BB} - R_{BA})\beta_{AB} n_{AB} - \beta_A R_{BA} n_A],$$

from which the relationships replacing (15) follows. Without writing it down explicitly, let us note that the tensor $\mathbb{D}$ turns out to be almost symmetric if

$$\beta_B R_{AB}\, n_B \ll \beta_{AB}\, n_{AB}, \quad \beta_A R_{BA} n_A \ll \beta_{AB}\, n_{AB}.$$

The error in the approach developed in [14] for which the two considered cases of intramolecular correlation in the gas phase, corresponding to perfectly different momentum distri-

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*Here and below we have in mind the bound state belonging to a discrete energy spectrum for a fixed center of mass, and not the virtual groups of Mayer expansions when speaking about the complexes.

butions substantially assumed identical, is evident from the above. In this connection, let's again emphasize the difference between the molecular complexes being understood as bound states, and the groups of Mayer expansions of the statistical sum of a nonideal gas.

The results obtained are extended trivially to the case of simultaneously taking account of the nonideality and the presence of complexes (we shall not write down the sufficiently awkward expressions to be obtained).

In concusion, let us note that the possibility of obtaining relations between the diffusion tensor components at the crossing point U (as well as in the domain outside the crossing, as is necessary for a more accurate study of the asymptotic of the solution (1) governing the composition of the grown seeds) for different specific models is actually based on an exact calculation of the dependence of the kinetic coefficients on the gas phase parameters. This permits the hope that relations diminishing the number of independent components of the diffusion tensor will be obtained successfully even in other problems where one of the phases is a weakly monideal gas, which will substantially facilitate the problem of calculating them from experimental results.

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