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Colloquium on Gauge Transformations for Thermodynamic Fluxes and Thermal Diffusion

Denis S. Goldobin

Department of Mathematics, University of Leicester, Leicester LE1 7RH, UK
Institute of Continuous Media Mechanics, UB RAS, Perm 614013, Russia
Department of Theoretical Physics, Perm State University, Perm 614990, Russia

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Abstract: We discuss the molecular diffusion transport in dilute liquid solutions under non-isothermal conditions. This discussion is actualized by an occurring misinterpretation of thermodynamic transport equations written in terms of chemical potential. Our treatment is based on the consideration of the entropy production.

Keywords: dilute solutions; thermodynamic transport cross-effects; thermal diffusion

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1. Introduction

In this paper we discuss the molecular diffusion transport in infinitely dilute liquid solutions under non-isothermal conditions. This discussion is motivated by an occurring misinterpretation of thermodynamic transport equations written in terms of chemical potential in the presence of temperature gradient. The transport equations contain the contributions owned by a gauge transformation related to the fact that chemical potential is determined up to the summand of form $(AT + B)$ with arbitrary constants A and B, where constant A is owned by the entropy invariance with respect to shifts by a constant value and B is owned by the potential energy invariance with respect to shifts by a constant value. The coefficients of the cross-effect terms in thermodynamic fluxes are contributed by this gauge transformation and, generally, are not the actual cross-effect physical transport coefficients. Our treatment is based on consideration of the entropy balance (e.g., see [1–3]) and suggests a promising hint for attempts of evaluation of the thermal diffusion constant from the first principles.

We also comment on impossibility of the "barodiffusion" for dilute solutions, understood in a sense of diffusion flux driven by the pressure gradient itself. When one speaks of "barodiffusion" terms in literature [3], these terms typically represent the drift in external potential force field (e.g., electric or gravitational fields), where in the final equations the specific force on molecules is substituted with an expression with the hydrostatic pressure gradient this external force field produces. Obviously, the interpretation of the latter as "barodiffusion" is fragile and may hinder the accounting for the diffusion fluxes produced by the pressure gradient itself.

2. Non-isothermal diffusion in the external potential

We wish to rederive the diffusion current of solutes in non-isothermal solvents using the basic thermodynamics and Onsager's principle [1,2]. We focus on the case of infinitely dilute solutions. We start from the first thermodynamic law for a two-component solution,

$$dU = T\,dS - P\,dV + \sum_{j=1,2} \mu_j\,dN_j\,. \tag{1}$$

Here the standard notations are used. S is the entropy of the system, U is the internal energy, V is the volume, N_1, N_2 and μ_1, μ_2 are respectively the number of particles and chemical potentials of the solvent and solute (in what follows the indices 1 and 2 denote correspondingly the solvent and solute). The number densities of particles are $n_j = N_j/V$. We consider dilute solutions, $n_2 \ll n_1$ (which is typical for solutions of gas in liquid). For a dilute solution, molecules of solute do not interact with each other and one can neglect the variations of the volume related to redistribution of the solute, which implies $v_1 N_1 + v_2 N_2 = V$, where v_j is the volume occupied by the molecule of sort j. We assume that liquid is incompressible, so that $V = \mathrm{const}$ and $v_{1,2} = \mathrm{const}$. Therefore, in all transport processes the condition $v_1 dN_1 + v_2 dN_2 = dV = 0$, implies the relation $dN_1 = -(v_2/v_1)\,dN_2$. We also assume that for a small variation of liquid density, due to thermal expansion, this relation holds true. Hence, we treat the variation of S as a function of U, n_1, and n_2 for the fixed volume V.

Using the specific quantities $u = U/V$ and $s = S/V = s(u, n_1, n_2)$ we write for a near-equilibrium system

$$\frac{dS}{dt} = \frac{d}{dt}\int\limits_V s\,dV = \int\limits_V \frac{\partial s}{\partial t}dV = \int\limits_V \left(\left(\frac{\partial s}{\partial u}\right)_{n_1,n_2} \frac{\partial u}{\partial t} + \left(\frac{\partial s}{\partial n_1}\right)_{u,n_2} \frac{\partial n_1}{\partial t} + \left(\frac{\partial s}{\partial n_2}\right)_{u,n_1} \frac{\partial n_2}{\partial t} \right) dV\,.$$

Here the subscripts of derivatives indicate the variables kept constant. From Eq. (1) we obtain

$$\left(\frac{\partial S}{\partial U}\right)_{V,N_1,N_2} = \frac{1}{T}\,, \quad \left(\frac{\partial S}{\partial N_1}\right)_{U,V,N_2} = -\frac{\mu_1}{T}\,, \quad \text{and} \quad \left(\frac{\partial S}{\partial N_2}\right)_{U,V,N_1} = -\frac{\mu_2}{T}\,.$$

The first derivative in the above equation is identical to $(\partial s/\partial u)_{n_1,n_2} = 1/T$, the other two, with respect to n_j, may be combined to yield

$$\begin{aligned}\left(\frac{\partial s}{\partial n_1}\right)_{u,n_2} dn_1\big|_V + \left(\frac{\partial s}{\partial n_2}\right)_{u,n_1} dn_2\big|_V &= \frac{1}{V}\left(\left(\frac{\partial S}{\partial N_1}\right)_{U,V,N_2} dN_1\big|_V + \left(\frac{\partial S}{\partial N_2}\right)_{U,V,N_1} dN_2\big|_V \right) \\ &= \frac{1}{V}\left(\left(-\frac{\mu_1}{T}\right) dN_1\big|_V + \left(-\frac{\mu_2}{T}\right) dN_2\big|_V \right) = -\frac{1}{V}\left(\frac{\mu_2}{T} - \frac{v_2}{v_1}\frac{\mu_1}{T}\right) dN_2\big|_V = -\frac{\mu_2 - (v_2/v_1)\mu_1}{T} dn_2\,,\end{aligned}$$

where we used the incompressibility condition $dN_1 = (v_2/v_1)dN_2$. Hence,

$$\frac{dS}{dt} = \int\limits_V \left(\frac{1}{T}\frac{\partial u}{\partial t} + \left(-\frac{\tilde{\mu}_2}{T} \right) \frac{\partial n_2}{\partial t} \right) dV \,,$$

where $\tilde{\mu}_2 = \mu_2 - (v_2/v_1)\mu_1$. Note, that the effective chemical potential $\tilde{\mu}$ has been also used in Ref. [4] for thermodynamical treatment of the thermodiffusion effect. Hereafter for various thermodynamic variables x_j we employ the notation $\tilde{x}_2 = x_2 - (v_2/v_1)x_1$. The time derivatives in the last equations are related to the corresponding fluxes as $(\partial u/\partial t) = -\nabla \cdot \vec{J}_u$ and $(\partial n_2/\partial t) = -\nabla \cdot \vec{J}_{n_2}$, where $\vec{J}_u$ and $\vec{J}_{n_2}$ are the fluxes of u and n_2, respectively. Hence we obtain

$$\frac{dS}{dt} = \int\limits_V \left(-\frac{1}{T}\nabla \cdot \vec{J}_u + \frac{\tilde{\mu}_2}{T}\nabla \cdot \vec{J}_{n_2} \right) dV \,.$$

For an isolated system (with vanishing fluxes on the boundary) the integration by parts yields

$$\frac{dS}{dt} = \int\limits_V \left(\vec{J}_u \cdot \nabla\frac{1}{T} + \vec{J}_{n_2} \cdot \nabla\left(-\frac{\tilde{\mu}_2}{T} \right) \right) dV \,. \tag{2}$$

For near-equilibrium systems the fluxes are linear in gradients, that is

$$\begin{pmatrix} \vec{J}_u \\ \vec{J}_{n_2} \end{pmatrix} = \mathbf{A} \cdot \begin{pmatrix} \nabla(1/T) \\ \nabla(-\tilde{\mu}_2/T) \end{pmatrix} ,$$

where $\mathbf{A}$ is the matrix of the respective transport coefficients. The positivity of dS/dt in Eq. (2) for any states of the system requires matrix $\mathbf{A}$ to have only positive eigenvalues. In particular, the absence of complex eigenvalues implies $\mathbf{A}$ to be symmetric;

$$\vec{J}_u = K\nabla\frac{1}{T} + \alpha n_2 \nabla\left(-\frac{\tilde{\mu}_2}{T} \right) , \tag{3}$$

$$\vec{J}_{n_2} = \alpha n_2 \nabla\frac{1}{T} + \frac{Dn_2}{k_B}\nabla\left(-\frac{\tilde{\mu}_2}{T} \right) , \tag{4}$$

where (K/T^2) is the heat conductivity, D is the molecular diffusivity, k_B is Boltzmann constant, and α is the coefficient which describes the cross-currents. Coefficient α should not be mistaken for the thermal diffusion constant [3]. Note, that writing Eq. (3) we have essentially exploited the Onsager's principle [1,2]. Then Eq. (2) reads

$$\frac{dS}{dt} = \int\limits_V \left[K\left(\nabla\frac{1}{T} \right)^2 - 2\alpha n_2 \nabla\frac{1}{T} \cdot \nabla\frac{\tilde{\mu}_2}{T} + \frac{Dn_2}{k_B}\left(\nabla\frac{\tilde{\mu}_2}{T} \right)^2 \right] dV \,.$$

The entropy production condition $dS/dt > 0$ for any non-equilibrium state requires the quadratic form of the gradients $\nabla(1/T)$ and $\nabla(\tilde{\mu}_2/T)$ in the above integrand to be positive. This yields the condition for the coefficients, $KD > \alpha^2 k_B n_2$, which is surely fulfilled for dilute solutions, $n_2 \ll 1$, even when $\alpha > DT$.

The above derivation is based on the general thermodynamic relations. To understand the microscopic meaning of the coefficient α we consider the microscopic expression for the energy flux $\vec{J}_u$, which is composed by the kinetic transfer with molecules and the phonon-mediated energy flux $\vec{J}_{\rm Ph}$,

$$\vec{J}_u = u_1\vec{J}_{n_1} + u_2\vec{J}_{n_2} + \vec{J}_{\rm Ph}\,,$$

where u_j is the internal energy per one molecule of sort j and $\vec{J}_{n_j}$ is the respective particle flux. Making use of relation $\vec{J}_{n_1} = -(v_2/v_1)\vec{J}_{n_2}$, we find $u_1\vec{J}_{n_1} + u_2\vec{J}_{n_2} = \tilde{u}_2\vec{J}_{n_2}$, where $\tilde{u}_2 = u_2 - (v_2/v_1)u_1$. Substitution of Eq. (4) into the latter expression for $\vec{J}_u$ yields

$$\vec{J}_u = \alpha n_2\tilde{u}_2\nabla\frac{1}{T} + \frac{Dn_2}{k_B}\tilde{u}_2\nabla\left(-\frac{\tilde{\mu}_2}{T}\right) + \vec{J}_{\rm Ph}\,.$$

The phonon energy flux $\vec{J}_{\rm Ph}$ is driven by temperature gradient and solute concentration inhomogeneity, because the concentration of guest molecules effects the spectrum of phonons and their scattering;

$$\vec{J}_{\rm Ph} = -\lambda_0\nabla T - \chi T\nabla n_2 = -\lambda_0\nabla T - \chi T n_2\nabla\ln n_2\,.$$

Here λ_0 is the heat conductivity of the solute-free liquid (indeed, for $n_2 = 0$ the net energy flux turns $-\lambda_0\nabla T$), coefficient χ can generally depend on the temperature, but is independent from n_2 for dilute solutions. To use the Onsager's principle we have to rewrite energy flux J_u in terms of natural thermodynamic forces $\nabla(1/T)$ and $\nabla(-\tilde{\mu}_2/T)$ (cf Eqs. (3) and (4)). We write the chemical potential in the following form:

$$\mu_2 = k_BT\ln n_2 + \Delta\mu_2\,,$$

where $\Delta\mu_2 = \mu_2 - k_BT\ln n_2$ is the sum of the ideal part of the chemical potential, which depends on the internal degrees of freedom of the gas molecule, of the non-ideal part, describing the interactions with the solvent and of the part, containing the local pressure; it is important that for dilute solutions $\Delta\mu_2$ does not depend on n_2, see e.g. [4]. For dilute solutions $|\nabla n_1|/n_1 \ll |\nabla n_2|/n_2$ and we can write

$$\nabla\ln n_2 = \nabla\frac{\tilde{\mu}_2 - \Delta\tilde{\mu}_2}{k_BT} = -\frac{1}{k_B}\nabla\left(-\frac{\tilde{\mu}_2}{T}\right) - \frac{\partial}{\partial T}\left(\frac{\Delta\tilde{\mu}_2}{k_BT}\right)\nabla T\,.$$

Thus, the energy flux reads

$$\vec{J}_u = \left(\lambda_0T^2 - \chi T^3 n_2\frac{\partial}{\partial T}\frac{\Delta\tilde{\mu}_2}{k_BT} + \alpha n_2\tilde{u}_2\right)\nabla\frac{1}{T} + \frac{(D\tilde{u}_2 + \chi T)n_2}{k_B}\nabla\left(-\frac{\tilde{\mu}_2}{T}\right).$$

Comparing the latter equation for $\vec{J}_u$ with Eq. (3), one finds $K = \lambda_0T^2 - \chi T^3 n_2(\partial/\partial T)(\Delta\tilde{\mu}_2/k_BT) + \alpha n_2\tilde{u}_2$ and

$$\alpha = \frac{D\tilde{u}_2 + \chi T}{k_B}\,.$$

Hence, the solute flux is

$$\begin{aligned}\vec{J}_{n_2} &= -Dn_2\left[-\left(\frac{\chi T}{k_BD} + \frac{\tilde{u}_2}{k_B}\right)\nabla\frac{1}{T} + \nabla\frac{\tilde{\mu}_2}{k_BT}\right]\\ &= -Dn_2\left[-\frac{\chi T}{k_BD}\nabla\frac{1}{T} + \nabla\frac{\tilde{\mu}_2 - \tilde{u}_2}{k_BT} + \frac{\nabla\tilde{u}_2}{k_BT}\right]. \qquad (5)\end{aligned}$$

Using the specific heat capacity of the solvent $c_{V,1}$ and the solute $c_{V,2}$, which do not depend on n_2 for dilute solutions, we write, $\tilde{u}_2 = \tilde{u}_{2,0} + \int^T \tilde{c}_{V,2}(T')dT' + \tilde{\phi}_2$, where $\tilde{u}_{2,0}$ does not depend on temperature and ϕ_j is the potential energy of the molecule of sort j ($j = 1,2$) in the external field, e.g. gravity. Further, for dilute solutions with negligible thermal expansion $(\partial v_j/\partial T) \ll (v_j/T)$—which holds nearly true for the aqueous solution of chemically inert gases—one can as well find $\tilde{\mu}_2 = T\tilde{S}_{0,2} + T\int^T (\tilde{c}_{V,2}(T')/T')\, dT' + \tilde{\phi}_2$, where $\tilde{S}_{0,2}$ is nearly independent from temperature and pressure. Finally, for dilute solutions, where $|\nabla n_1|/n_1 \ll |\nabla n_2|/n_2$, Eq. (5) takes the form

$$\vec{J}_{n_2} = -Dn_2 \left[\frac{\nabla n_2}{n_2} + \frac{\chi}{k_B T D} \nabla T + \frac{\nabla \tilde{\phi}_2}{k_B T} \right]. \tag{6}$$

Using $\tilde{m}_2 \vec{g} = -\nabla \tilde{\phi}_2$ for the gravitational field, we recast the above equation into the form

$$\vec{J}_{n_2} = -Dn_2 \left[\frac{\nabla n_2}{n_2} + \alpha_T \frac{\nabla T}{T} - \frac{\tilde{M}\vec{g}}{RT} \right]. \tag{7}$$

Here $\tilde{M} = M_2 - (v_2/v_1)M_1$, M_j is the molar mass, and

$$\alpha_T = \frac{\chi}{k_B D} \tag{8}$$

is the thermal diffusion constant. The thermodynamic expression for the thermal diffusion constant has been also reported in Ref. [4], where it has been evaluated with different approach.

Theoretical study [4] estimates the isotope part of thermal diffusion

$$\alpha_{T,\mathrm{isot}} = \frac{3}{4} \ln \frac{M_2 v_1}{M_1 v_2}$$

to be strictly temperature-independent. This analytic result underestimates the experimental results [5] on the isotopic part approximately by factor 3.

3. Discussion and Conclusion

We would like to emphasize for non-isothermal systems that in the thermodynamic fluxes (3) and (4) the term $\nabla(-\tilde{\mu}_2/T)$ describes not merely the Fickian diffusion, as well as the terms with α are not purely the thermodynamic cross-fluxes. These terms are mutually interweaved and the terms with α can be present in the absence of any thermodynamic cross-effects, purely pertaining to the gauge transformation associated with the invariance of the chemical potential to addition of $(AT + B)$ with arbitrary constants A and B.

With relation between of α_T and χ (Eq. (8)), one can consider possibility to derive the thermodynamic expression for the thermal diffusion constant, dealing not with the current of specie molecules but with the thermal motion energy flux $\vec{J}_{\mathrm{Ph}}$ across the volume with maintained temperature and specie concentration gradients.

At the very beginning of the derivation procedure we excluded the contributions to entropy production owned by the volume change, $(\partial S/\partial V)_{U,N_1,N_2}$, which would bring-in the thermodynamic flux driven by the thermodynamic force $\nabla(P/T)$. This compressibility-related force was excluded by virtue of the vanishing effect of the solute redistribution on the system volume for infinitely dilute solutions. The cross-current associated to $\nabla(P/T)$ is the barodiffusion, which, therefore, vanishes for dilute solutions we consider. However, frequently in literature (e.g., [3]), the term describing the drift in an external potential force field, i.e. the last term in Eq. (6), is recast in terms of the hydrostatic pressure gradient produced by the force field. For instance, in [3], $\vec{g}$ is substituted with $\rho^{-1}\nabla P$. After this substitution, all the terms in the expression for the molecular diffusion flux are referred to as barodiffusion. We would like to warn against such a usage of the notion of barodiffusion and suggest to distinguish between the fluxes driven by external force fields and the flux driven by thermodynamic force $\nabla(P/T)$, meaning only the latter to pertain to barodiffusion. The interpretation of the former as barodiffusion is fragile and may hinder the accounting for the diffusion fluxes produced by the pressure gradient itself.

The calculation of the thermal diffusion constant from the first principles is actualized by the lack of experimental data on the values of this constant for weakly soluble gases, such as methane, carbon dioxide, etc., and importance of thermal diffusion of these gases in marine sediments [6–8].

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