# AN INTRODUCTION TO THE ONSAGER RECIPROCAL RELATIONS

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An important question stimulated the fundamental development of multicomponent transport theory: How many independent transport properties characterize coupled diffusion? The answer was provided by Onsager, who used fluctuation theory to find reciprocal relations among the transport coefficients. The Onsager reciprocal relation connects thermodynamics, transport theory, and statistical mechanics. To illustrate this connection, a relation is derived here for the Soret and Dufour effects in binary ideal-gas diffusion.

Reciprocal relations may be appropriately introduced in graduate courses on thermodynamics, transport, or statistical mechanics. The subject can provide a capstone to a thermodynamics course, where it shows how thermodynamic methods extend to transport processes. In a transport course, the eventual development of reciprocal relations can motivate a formulation of thermodynamically consistent multicomponent transport laws.

Statistical mechanics is probably the most relevant field. As well as showing the importance of fluctuation correlations when analyzing systems near equilibrium, the reciprocal relation introduces several elementary properties of equilibrium correlations. In a statistical context, the derivation also provides a means to review topics from thermodynamics and transport, illustrating how these seemingly disparate fields relate.

This discussion follows the method that Onsager employed in his seminal papers on irreversible processes.[1, 2] By inspection of the system's local energy dissipation, macroscopic flux laws are developed to relate diffusional fluxes to thermodynamic driving forces. Conservation laws for heat and mass then provide a set of differential equations that describes how macroscopic nonequilibrium states evolve. The Onsager regression hypothesis allows this system of equations to be applied to the time evolution of correlations between microscopic fluctuations of composition and temperature. A reciprocal relation arises from the principle of microscopic reversibility, which requires symmetry of equilibrium fluctuation correlations. Equilibrium statistical mechanics can then be used to express the reciprocal relation in terms of macroscopic properties.

Flux laws that account for the Soret and Dufour effects in a binary gas include four phenomenological properties. These are the binary diffusivity $\mathscr{D}_{12}$, the thermal conductivity k, and two additional coefficients for the Soret and Dufour effects. Onsager's procedure provides a reciprocal relation among them, showing that only three are independent.

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## FLUX LAWS

Flux laws must satisfy several requirements. Near equilibrium, fluxes are linear with respect to diffusion driving forces, and vice versa. Also, when all forces are zero, all fluxes are zero. Proper diffusion laws should involve kinematically independent fluxes and thermodynamically independent driving forces.

The diffusion of component i can be induced by gradients of chemical potential $\mu_i$ (Fickian diffusion), temperature T (the Soret effect), or pressure p (centrifugation). A generalized thermodynamic force which drives the flux of i is

$$\mathbf{d}_i = -c_i\left(\nabla\mu_i + \bar{S}_i\nabla T - \frac{M_i}{\rho}\nabla p\right) \tag{1}$$

where $c_i$ is the concentration of i, $M_i$ its molar mass, and $\bar{S}_i$ its partial molar entropy; ρ is the density. The term with $\nabla p$ corrects for the equilibrium chemical potential gradient of pure i in a gravitational or centrifugal field; the term with $\nabla T$ makes $\mathbf{d}_i$ independent of the reference state for entropy in $\mu_i$. Because the Gibbs-Duhem equation requires that $\sum_i \mathbf{d}_i = 0$, the number of independent mass-transfer driving forces is one fewer than the number of components.

For a binary system, the entropy-continuity equation is

$$\rho\frac{D\hat{S}}{Dt} = -\nabla\cdot\left(\frac{\mathbf{q}'}{T} + \bar{S}_1\mathbf{J}_1 + \bar{S}_2\mathbf{J}_2\right) + g \tag{2}$$

where t is time, $\hat{S}$ is the specific entropy, $\mathbf{J}_i$ is the molar flux of i relative to the mass-average velocity, and g is the local rate of entropy generation; $\mathbf{q}'$ is a derived quantity, obtained by subtracting the latent heat carried by diffusing species from the total heat flux.* This equation can be manipulated with the material, momentum, and energy continuity equations, the first law of thermodynamics, and vector identities to eliminate all of the substantial derivatives. The energy dissipation per unit volume, Tg, then takes the form†

$$Tg = -\mathbf{q}'\cdot\nabla\ln T + (\mathbf{v}_1 - \mathbf{v}_2)\cdot\mathbf{d}_1 \tag{3}$$

where $\mathbf{v}_1$ and $\mathbf{v}_2$ are the component velocities. Thus $\mathbf{q}'$ and $-\nabla \ln T$ arise naturally as a flux and driving force associated with heat transfer.

To write general flux laws for an isotropic system, the two fluxes in Eq. (3) can be related to the two driving forces in linear, homogeneous relations, with four phenomenological proportionality constants (*i.e.*, diffusion coefficients), $L_{qq}$, $L_{q1}$, $L_{1q}$, and $L_{11}$:

$$\begin{aligned}\mathbf{q}' &= -L_{qq}\nabla\ln T + L_{q1}\mathbf{d}_1\\ \mathbf{v}_1 - \mathbf{v}_2 &= -L_{1q}\nabla\ln T + L_{11}\mathbf{d}_1\end{aligned} \tag{4}$$

Here $L_{1q}$ accounts for the Soret effect, and $L_{q1}$, the Dufour effect. (In an anisotropic system, each of the $L_{ij}$ would generally be a tensor.)

For a binary ideal gas at uniform pressure, Eqs. (4) become

$$\begin{aligned}\mathbf{q}' &= -k\nabla T - RTc_T L_{q1}\nabla y_1\\ \mathbf{v}_1 - \mathbf{v}_2 &= -L_{1q}\nabla\ln T - \frac{\mathscr{D}_{12}}{y_1 y_2}\nabla y_1\end{aligned} \tag{5}$$

where $y_i$ is the mole fraction of component i and $c_T = c_1 + c_2$. In Eqs. (5), $L_{qq}/T$ has been identified as k (the thermal conductivity), and RT $L_{11}$ as $\mathscr{D}_{12}/y_1y_2$ (proportional to the binary diffusivity), so that Fourier's and Fick's laws appear when one of the driving forces is absent. The reciprocal relation allows a restatement of these flux laws in terms of only three transport properties.

## TRANSPORT AND MOMENTS

Later it will be important to know how conservation laws for mass and energy control system evolution. This can be elucidated by describing a transient macroscopic variation within the system. General solutions of the continuum transport equations for arbitrary initial variations of composition and temperature specify how composition changes, with the assumption in the present example that the system is at uniform pressure.

Continuity equations govern both components and the thermal energy. The choice of system dictates an isobaric energy equation. Due to isotropy, it is sufficient to treat diffusion in one direction. To simplify the analysis, consider a one-dimensional slab of length L. Assume that displacements from equilibrium are sufficiently small that the governing equations can be expressed in forms linearized around a final equilibrium state, denoted with a superscript ∞.

A difference between the two equations that express component continuity yields a single equation in terms of $(\mathbf{v}_1 - \mathbf{v}_2)$, and the sum of mole fractions, $y_1 + y_2 = 1$, can be used to eliminate derivatives of $y_2$. Thus two transient equations of the form

$$\begin{aligned}\frac{1}{T^\infty}\frac{\partial T}{\partial t} &= \frac{k^\infty}{c_T^\infty \tilde{C}_p^\infty T^\infty}\frac{\partial^2 T}{\partial x^2} + \frac{RL_{q1}^\infty}{\tilde{C}_p^\infty}\frac{\partial^2 y_1}{\partial x^2}\\ \frac{\partial y_1}{\partial t} &= \frac{y_1^\infty y_2^\infty L_{1q}^\infty}{T^\infty}\frac{\partial^2 T}{\partial x^2} + \mathscr{D}_{12}^\infty\frac{\partial^2 y_1}{\partial x^2}\end{aligned} \tag{6}$$

govern $y_1$ and T. Here x denotes the position within the slab.

It is preferable to simplify Eqs. (6) so that they depend only

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* *If the total heat flux is q, then* $q' = q - \sum_i \bar{H}_i J_i$, *where* $\bar{H}_i$ *is the partial molar enthalpy of i.*

† *For a simple example of this procedure, see Bird, Stewart, and Lightfoot.*[3] *A detailed derivation is given by Hirschfelder, Curtiss, and Bird.*[4]

on time. To do this Onsager examined the moments of $y_1$ and T—that is, their distributions integrated over position. The slab is closed and insulated; its total contents of material and energy are constant in time. This manifests itself as a property of the moments, such as

$$\int_0^L \left[y_1(t,x) - y_1^\infty\right] dx = 0 \tag{7}$$

A similar equation holds for $[T(t,x) - T^\infty]$.

Fourier series obey the properties of the moments and can be used to describe $y_1$ and T. Cosine series meet the additional requirement that both fluxes are zero at x = 0 and L. Series expansions of the temperature and composition distribution are given by

$$\begin{aligned} \frac{T - T^\infty}{T^\infty} &= \sum_{m=1}^{\infty} a_m(t)\cos\left(\frac{m\pi x}{L}\right) \\ y_1 - y_1^\infty &= \sum_{m=1}^{\infty} b_m(t)\cos\left(\frac{m\pi x}{L}\right) \end{aligned} \tag{8}$$

These have been written so that both $a_m$ and $b_m$ are dimensionless.

Substitution of Eqs. (8) into Eqs. (6) yields a system of ordinary differential equations. To separate the Fourier components by wave number m, multiply each equation by $\cos(m\pi x/L)$ and integrate with respect to x from 0 to L. The orthogonality of the cosine function shows that different harmonics are decoupled, and one obtains

$$\begin{aligned} \frac{da_m}{d\tau} &= -\frac{k^\infty}{c_T^\infty \tilde{C}_p^\infty} a_m - \frac{RL_{q1}^\infty}{\tilde{C}_p^\infty} b_m \\ \frac{db_m}{d\tau} &= -y_1^\infty y_2^\infty L_{1q}^\infty a_m - \mathscr{D}_{12}^\infty b_m \end{aligned} \tag{9}$$

where $\tau = m^2\pi^2 t/L^2$. Eqs. (9) can be solved directly, yielding functions that describe how the amplitudes of arbitrary initial distributions decay with time. This general formulation of the macroscopic problem sets the stage for statistical analysis.

## STATISTICAL MECHANICS AND TIME CORRELATIONS

At macroscopic equilibrium, constant values $T = T^\infty$ and $y_1 = y_1^\infty$ prevail throughout the slab. This view belies the microscopic reality. As time passes, particles move randomly, causing local variations in the temperature and composition. Imagine taking a snapshot of the slab at equilibrium and mapping out T and $y_1$ with position; the distributions will be nearly, but not exactly, uniform. Such an instantaneous sample is called a *fluctuation state*. Equilibrium itself is an aggregate of transient fluctuation states.

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Onsager's *regression hypothesis* states that *fluctuations evolve according to the laws that govern macroscopic variations*. In practice, the regression hypothesis allows $a_m$ and $b_m$ to be used as descriptors of microscopic states. For instance, it says that Eqs. (9), which govern macroscopic variations, also apply to transient fluctuation states.

The total set of available fluctuation states is called the *ensemble*. In a fluctuating equilibrated system, the macroscopic properties differ from those of a system with uniformly distributed intensive properties. Averages over the ensemble of fluctuation states quantify how the macroscopic properties of a fluctuating system differ from those of a uniform system.

Correlations measure the degree to which two attributes of a system vary together. The ensemble average of a pair of fluctuations, such as $\langle a_m b_m \rangle$, indicates how $a_m$ and $b_m$ are correlated within the ensemble—that is, for a fluctuation state selected at random, how much one expects the value of $a_m$ to correspond with that of $b_m$. With the regression hypothesis, the equations from transport theory can also be used to analyze fluctuation correlations.

The average $\langle a_m(\tau_0) b_m(\tau_0) \rangle$ defines the *initial correlation* between $a_m$ and $b_m$ at time $\tau_0$. This quantifies the degree to which two fluctuations are expected to be correlated for instantaneous observations of the system. A more general correlation involves fluctuations observed at different times. The *time correlation* between $a_m$ at $\tau_0$ and $b_m$ at a later instant $\tau_0 + \tau$,

$$C_{ab}(\tau) = \langle a_m(\tau_0) b_m(\tau_0 + \tau) \rangle \tag{10}$$

is expressed with the shorthand notation $C_{ab}(\tau)$. Note that $C_{ab}(0)$ represents the initial correlation, which is also written with the shorthand notation $C_{ab}^0$.

To apply the regression hypothesis to Eqs. (9), multiply each successively by $a_m(\tau_0)$ and $b_m(\tau_0)$, then take the ensemble average,‡ yielding four differential equations for the time correlations. Then find solutions of this system for arbitrary initial conditions. With the simplifying notation

$$\begin{aligned} \alpha_\pm &= \frac{k^\infty}{2c_T^\infty \tilde{C}_p^\infty} \pm \frac{\mathscr{D}_{12}^\infty}{2} \quad \text{and} \\ \alpha_0 &= \sqrt{\alpha_-^{\,2} + \frac{y_1^\infty y_2^\infty R L_{1q}^\infty L_{q1}^\infty}{\tilde{C}_p^\infty}} \end{aligned} \tag{11}$$

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‡ *For the time being it is sufficient to note that* $\langle\ \rangle$ *is a linear operator. The initial correlations section discusses the averaging operation in more detail.*

the time correlations become

$$
\begin{aligned}
C_{aa}(\tau) &= C^0_{aa} e^{-\alpha_+\tau}\left[\cosh(\alpha_0\tau) - \frac{\alpha_-}{\alpha_0}\sinh(\alpha_0\tau)\right] \\
&\quad - C^0_{ab}\frac{L^\infty_{q1}R}{\alpha_0\tilde{C}^\infty_p} e^{-\alpha_+\tau}\sinh(\alpha_0\tau) \\
C_{ba}(\tau) &= C^0_{ba} e^{-\alpha_+\tau}\left[\cosh(\alpha_0\tau) - \frac{\alpha_-}{\alpha_0}\sinh(\alpha_0\tau)\right] \\
&\quad - C^0_{bb}\frac{L^\infty_{q1}R}{\alpha_0\tilde{C}^\infty_p} e^{-\alpha_+\tau}\sinh(\alpha_0\tau) \\
C_{ab}(\tau) &= C^0_{ab} e^{-\alpha_+\tau}\left[\cosh(\alpha_0\tau) + \frac{\alpha_-}{\alpha_0}\sinh(\alpha_0\tau)\right] \\
&\quad - C^0_{aa}\frac{L^\infty_{1q}y^\infty_1 y^\infty_2}{\alpha_0} e^{-\alpha_+\tau}\sinh(\alpha_0\tau) \\
C_{bb}(\tau) &= C^0_{bb} e^{-\alpha_+\tau}\left[\cosh(\alpha_0\tau) + \frac{\alpha_-}{\alpha_0}\sinh(\alpha_0\tau)\right] \\
&\quad - C^0_{ba}\frac{L^\infty_{1q}y^\infty_1 y^\infty_2}{\alpha_0} e^{-\alpha_+\tau}\sinh(\alpha_0\tau) \qquad (12)
\end{aligned}
$$

Initial correlations decay exponentially, with decay constants ($\alpha_+ + \alpha_0$) and ($\alpha_+ - \alpha_0$). (Thermodynamic stability requires that both constants be positive.)

## MICROSCOPIC REVERSIBILITY AND RECIPROCAL RELATIONS

In an equilibrium ensemble, time correlations have symmetry properties that lead to reciprocal relations. These properties arise from the principle of *microscopic reversibility.*

Onsager's interpretation of this principle is that, *at equilibrium, molecular processes occur with equal likelihood in the forward and reverse directions.* That is, the expectation that an event observed now will be followed $\tau$ later by a second event is the same as the expectation that it was preceded $\tau$ ago by the second event, or

$$\langle a_m(\tau_0)\, b_m(\tau_0+\tau)\rangle = \langle a_m(\tau_0)\, b_m(\tau_0-\tau)\rangle \qquad (13)$$

This property is also called *time-reversal symmetry.*[5]

Because equilibrium is a stationary condition, time correlations are insensitive to shifts of $\tau_0$ in Eq. 10. Replacement of $\tau_0$ with $\tau_0 + \tau$ leaves correlations unchanged. Thus

$$\langle a_m(\tau_0)\, b_m(\tau_0-\tau)\rangle = \langle a_m(\tau_0+\tau)\, b_m(\tau_0)\rangle \qquad (14)$$

which is also known as the principle of *time-translational invariance.*

With Eq. (13), the principle of time-translational invariance can be used to show

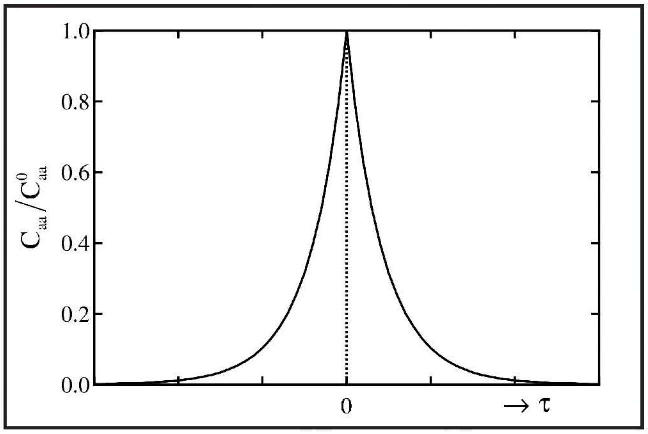

***Figure 1.*** *Qualitative behavior of the decay of correlation $C_{aa}$ with correlation time $\tau$.*

$$\langle a_m(\tau_0)\, b_m(\tau_0+\tau)\rangle = \langle a_m(\tau_0+\tau)\, b_m(\tau_0)\rangle$$
$$\text{or} \quad C_{ab}(\tau) = C_{ba}(\tau) \qquad (15)$$

which phrases the principle of microscopic reversibility: the expectation that a first event observed at $\tau_0$ will be followed $\tau$ later by a second event is the same as the expectation that the second event observed at $\tau_0$ will be followed $\tau$ later by the first.[6]

Figure 1 presents the qualitative behavior of time correlation $C_{aa}$. The regression hypothesis showed that correlations decay exponentially. The decay is symmetric in the forward and reverse directions because of microscopic reversibility.

A reciprocal relation is obtained directly from the statement of microscopic reversibility in Eq. (15). Equating $C_{ab}$ to $C_{ba}$ from Eq. (12) relates the transport properties to the initial correlations $C^0_{aa}$, $C^0_{bb}$, and $C^0_{ab}$ (= $C^0_{ba}$) through

$$L^\infty_{q1} = \frac{\tilde{C}^\infty_p y^\infty_1 y^\infty_2}{R}\left(\frac{C^0_{aa}}{C^0_{bb}}\right)L^\infty_{1q} + \left(\frac{\tilde{C}^\infty_p \mathscr{D}^\infty_{12}}{R} - \frac{k^\infty}{Rc^\infty_T}\right)\left(\frac{C^0_{ab}}{C^0_{bb}}\right) \qquad (16)$$

This is the most general statement of the reciprocal relation for thermal diffusion in an isotropic, isobaric, binary ideal-gas mixture. All four of the transport coefficients are involved. The result is independent of $\tau$ ; it is also independent of m, as shown shortly.

## INITIAL CORRELATIONS

To get the magnitudes of the initial correlations in terms of macroscopic quantities, Onsager applied statistical methods to equilibrium fluctuations, referencing Einstein's statement that *fluctuation states are equally probable.*[7] This axiom allows the probability density of fluctuation states in the ensemble to be simply related to a thermodynamic potential. Once the probability density is known, it can be used to compute ensemble averages.

Because the system in question here is adiabatic, the distribution of states within the ensemble is determined by the entropy S. The principle of equal probability shows that the entropy of a system with $\Omega$ available states is given by

$$\mathrm{S} = \mathrm{k_B} \ln \Omega \tag{17}$$

where $k_B$ is Boltzmann's constant. Correlations between fluctuations introduce some microscopic order; therefore, when the composition and temperature fluctuate in an adiabatic system, the entropy does as well. If entropy itself fluctuates, Eq. (17) suggests that the probability density of fluctuation states within the ensemble, $\rho$, can be written as

$$\rho = \frac{1}{\mathrm{N}} \exp\left(\frac{\mathrm{S}}{\mathrm{k_B}}\right) \tag{18}$$

where N is a normalization factor to make the sum of $\rho$ over all accessible S equal to unity.

The ensemble average of a property f, $\langle f \rangle$, is given by integrating $f\rho$ over all states (over all values of $a_m$ and $b_m$, at every m, at a given instant). For instance,

$$\mathrm{C}_{ab}^{0} = \left\langle a_m(\tau_0) b_m(\tau_0) \right\rangle \propto \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} a_m b_m \rho(\mathrm{S}) \, da_m \, db_m \tag{19}$$

To implement integrations like this one, S must be stated in terms of the fluctuation amplitudes $a_m$ and $b_m$.

In the present example of a binary ideal gas, the system entropy can be expressed as an integral over the slab volume. It depends on T and $y_1$ through§

$$\mathrm{S} = \mathrm{R} \int c_T^{\infty} \left[ \frac{\tilde{\mathrm{C}}_p^{\infty}}{\mathrm{R}} \ln \mathrm{T} - y_1 \ln y_1 - (1 - y_1) \ln (1 - y_1) - \ln p \right] d\mathrm{V} \tag{20}$$

For small displacements from uniform distributions, S can be found in terms of $a_m$ and $b_m$ as follows. Let $S^{\infty}$ be the system entropy when $y_1$ and T are uniform. Express $y_1$ and T in the integrand of Eq. (20) as linear perturbations around $y_1^{\infty}$ and $T^{\infty}$. Then insert the Fourier series from Eqs. (8) for the linear perturbations and perform the integration. Constant terms contribute to $S^{\infty}$, and linear terms vanish, leaving only quadratic terms. (For large systems, terms of higher than second order are negligibly small.) Thus

$$\mathrm{S}(\tau_0) = \mathrm{S}^{\infty} - \frac{n_T \mathrm{R}}{4} \sum_{m=1}^{\infty} \left[ \frac{\tilde{\mathrm{C}}_p^{\infty}}{\mathrm{R}} a_m^2(\tau_0) + \frac{1}{y_1^{\infty} y_2^{\infty}} b_m^2(\tau_0) \right] \tag{21}$$

where $n_T$ is the total number of gas molecules in moles. This form of S has the correct qualitative properties; any nonzero $a_m(\tau_0)$ or $b_m(\tau_0)$ lowers the entropy from its maximum value when $a_m(\tau_0) = b_m(\tau_0) = 0$.

By following the definition of the ensemble average, with $f = a_m(\tau_0) b_m(\tau_0)$ and $\rho$ given through Eqs. (18) and (21), one finds that the cross-correlations are zero,

$$\mathrm{C}_{ab}^{0} = \mathrm{C}_{ba}^{0} = 0 \tag{22}$$

The other initial correlations, found with $f = a_m(\tau_0) a_m(\tau_0)$ and $f = b_m(\tau_0) b_m(\tau_0)$, are

$$\mathrm{C}_{aa}^{0} = \frac{\mathrm{A}_m}{y_1^{\infty} y_2^{\infty}} \quad \text{and}$$

$$\mathrm{C}_{bb}^{0} = \frac{\mathrm{A}_m \tilde{\mathrm{C}}_p^{\infty}}{\mathrm{R}} \tag{23}$$

Note that they are always positive. In these expressions, $A_m$ is a constant, which depends in a rather complicated way on the coefficients in Eq. (21), as well as $S^{\infty}$ and the probability normalization factor N. More significantly, $A_m$ may depend on m—but its specific value is never needed because Eq. (16) involves only ratios of correlations. Thus the prefactor cancels, and the reciprocal relation is independent of the wavenumber.

Values of the initial correlations from Eqs. (22) and (23) can be inserted into Eq. (16), revealing that

$$\mathrm{L}_{q1} = \mathrm{L}_{1q} \tag{24}$$

This establishes the desired reciprocal relation. The transport coefficients for the Soret and Dufour effects equate.

Proper application of Onsager's principles, as demonstrated above, may not always lead to such a simple result. In general, a reciprocal relation yields only the same number of relationships among transport properties as a symmetry of the matrix **L**. The symmetry expressed by Eq. (24) arose from Eq. (16) in large part because the system is an ideal gas, for which the fluctuation correlations have particularly simple properties. When considering reciprocal relations for nonideal gases or liquids, activity coefficients must be incorporated into the constitutive laws for chemical potential. These additional thermodynamic relations make activity-coefficient gradients appear in Eqs. (5), and can lead the cross-correlations to be nonzero, complicating the analysis somewhat.[8] It has not been established conclusively that this complication leads to transport-coefficient asymmetry.

## DISCUSSION

Onsager reciprocal relations are a compelling topic for study because of the important physical concepts involved, the generality of their derivation, and the diverse fields which they interrelate.

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*§ For simplicity, the possible dependences of $c_T$ and $\tilde{C}_p$ on $y_1$ and T have been neglected while deriving Eq. (20).*

In this analysis, the mass-transfer driving forces were expressed in terms of mole fractions, and the flux law for mass transfer was expressed relative to the velocity of component 2. But Eq. (16) results if flux laws are written in terms of any other complete set of composition variables (mass fractions, molar concentrations, etc.), or with any other reference velocity for the fluxes (the mass-average velocity, number-average velocity, etc.). When linearizing around a uniform state, the same reciprocal relation is obtained no matter which variables are considered.

To find expressions for the initial correlations, the system was assumed to be adiabatic. For isothermal, isobaric systems one should express the probability density of states in terms of the Gibbs free energy; for isothermal systems with fixed volume, one should express $\rho$ in terms of the Helmholtz free energy. This does not affect reciprocal relations for ideal-gas mixtures, but in nonideal cases the thermodynamic potential chosen for ensemble averaging may affect the initial correlations.[8]

Another issue is that the initial correlations appear to have the same value at every m. Since m ranges to infinity, this seems to say that the sum of fluctuation correlations is infinite. In fact, the summations in Eq. (21) must terminate at some large value of m, where the wavelength of fluctuations approaches molecular dimensions. The macroscopic theoretical result which was used to derive Eq. (21) does not properly describe this regime.

The Onsager reciprocal relation is often cited as a general proof of cross-coefficient symmetry in coupled transport laws. It is important to realize that microscopic reversibility, which implies time-correlation symmetry, does not necessarily imply a consequent symmetry of macroscopic transport properties. Given thermodynamically rigorous transport laws, it may be correct to assert transport-coefficient symmetry in macroscopic transport models. But no statistical proof based on the regression hypothesis substantiates this assertion for the equations typically used to describe simultaneous heat, mass, momentum, and charge transport within nonideal, multicomponent solutions. This issue was first raised by Coleman and Truesdell[9] and has stood unresolved for almost 50 years. Recent attempts have been made to address the problem, but at present the discrepancy remains.[8, 10, 11]

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