

Addition to “Revised Formulation of Fick’s, Fourier’s, and Newton’s Laws for Spatially Varying Linear Transport Coefficients”

You-Yeon Won* and Doraiswami Ramkrishna

ACS Omega 2019, 4 (6), 11215–11222. DOI: 10.1021/acsomega.9b00736



Cite This: ACS Omega 2020, 5, 33484–33487



Read Online

ACCESS |



Metrics & More



Article Recommendations



Supporting Information

Regarding our previous publication entitled “Revised Formulation of Fick’s, Fourier’s, and Newton’s Laws for Spatially Varying Linear Transport Coefficients” (Won, Y.-Y.; Ramkrishna, D. ACS Omega 4, 11215–11222, 2019 (DOI: 10.1021/acsomega.9b00736)),¹ we wish to add short discussions on the following three issues: (1) the consistency of the revised Fick’s law equation with nonequilibrium thermodynamics, (2) the inapplicability of the revised Fourier’s law equation to solid systems, and (3) the consistency of the revised Fourier’s law equation with the postulate of positive local entropy production.

1. THE REVISED FICK’S LAW EQUATION CAN BE DERIVED WITHIN THE ESTABLISHED FRAMEWORK OF MODERN NONEQUILIBRIUM THERMODYNAMICS

In nonequilibrium thermodynamics, the original Fick’s law can be derived as follows. The diffusive flux of species 1 (solute) (j_1) in a binary mixture with species 2 (solvent) at constant temperature (T) is given as^{2,3}

$$j_1 = -\frac{L_{11}}{c_2 T} \nabla(\mu_1) \quad (1)$$

where L_{11} is the phenomenological coefficient, c_2 is the concentration of the solvent, and μ_1 is the chemical potential of the solute. Since $\mu_1 = f(c_1)$, the chemical potential gradient can be expressed in terms of the concentration gradient

$$\nabla(\mu_1) = \left(\frac{\partial \mu_1}{\partial c_1} \right)_{T,P,c_2} \nabla(c_1) \quad (2)$$

Substitution of this relation into the above flux equation (eq 1) gives the original Fick’s law expression

$$j_1 = -\frac{L_{11}}{c_2 T} \left(\frac{\partial \mu_1}{\partial c_1} \right)_{T,P,c_2} \nabla(c_1) = -D_1 \nabla(c_1) \quad (3)$$

Now let us assume that there exists another spatially varying variable (say, δ_1) rooted in the heterogeneity of the medium that influences the chemical potential, that is, $\mu_1 = f(c_1, \delta_1)$. Then the above chain rule equation (eq 2) is changed to

$$\nabla(\mu_1) = \left(\frac{\partial \mu_1}{\partial c_1} \right)_{T,P,c_2,\delta_1,\delta_2} \nabla(c_1) + \left(\frac{\partial \mu_1}{\partial \delta_1} \right)_{T,P,c_1,c_2,\delta_2} \nabla(\delta_1) \quad (4)$$

Accordingly, the Fick’s law equation becomes

$$j_1 = -\frac{L_{11}}{c_2 T} \left(\frac{\partial \mu_1}{\partial c_1} \right)_{T,P,c_2,\delta_1,\delta_2} \nabla(c_1) + -\frac{L_{11}}{c_2 T} \left(\frac{\partial \mu_1}{\partial \delta_1} \right)_{T,P,c_1,c_2,\delta_2} \nabla(\delta_1) \\ = -D_1 \nabla(c_1) - \Gamma_1 \nabla(\delta_1) \quad (5)$$

As discussed in our previous paper,¹ δ_1 can be the standard state chemical potential (μ_1°) or the activity coefficient (γ_1) of the solute, and both of these properties can be related to D_1 . One might question how a property of equilibrium (e.g., chemical potential) can be related to a property of kinetics (e.g., diffusivity). However, we note that it is a prevailing view in modern statistical mechanics that the magnitudes of equilibrium fluctuations of a system determine how fast the system approaches equilibrium. This “fluctuation-dissipation” theorem allows one to determine the diffusivity, viscosity, and other transport properties from equilibrium fluctuations. For instance, the equations collectively known as the Green–Kubo relations relate the diffusion coefficient to the equilibrium velocity correlation function, and the friction coefficient to the equilibrium force correlation function;⁴ this concept was also implicit in eq 46 of our previous paper.¹ There are other established concepts that reflect the thermodynamic character of the diffusivity (the chemical diffusivity defined by the Fick’s first law), such as the negative diffusivity in spinodally decomposing systems⁵ and the Rosenfeld correlation between diffusivity and excess entropy.⁶ Now, if we let $\delta_1 = D_1$, the above equation reduces to a form that is similar to the revised Fick’s law formula proposed in our paper

$$j_1 = -D_1 \nabla(c_1) - \Gamma_1 \nabla(D_1) \quad (6)$$

Received: June 15, 2020

Published: December 15, 2020



Here, the transport coefficient of the second term Γ_1 represents a quantity in units of concentration. To demonstrate the equivalence of the two quantities, Γ_1 and c_1 , let us further assume that the standard state chemical potential of the solute (μ_1°) is directly related to its diffusivity (D_1) through the following phenomenological relation

$$\mu_1^\circ = RT \ln\left(\frac{D_1}{D_o}\right) \quad (7)$$

where a unit of diffusivity (D_o) is introduced to make the argument of the logarithmic function unitless; in the pH-phoretic situation discussed in ref 7, for instance, μ_1° is indeed expected to vary spatially because of the spatially varying hydration state of the solute molecules (particles). The logarithmic dependence of μ_1° on D_1 is assumed in analogy to the logarithmic dependence of μ_1 on c_1 (see eq 8 below) and due to the fact that the gradients of c_1 and D_1 both contribute symmetrically to the diffusion process (see eqs 8 and 9 of our previous paper¹). On the basis of eq 7, the solute's chemical potential can be written, in the dilute limit ($\gamma_1 = 1$), as

$$\mu_1 = \mu_1^\circ + RT \ln\left(\frac{c_1}{c_o}\right) = RT \ln\left(\frac{D_1 c_1}{D_o c_o}\right) \quad (8)$$

where c_o is the total concentration of all molecules, which is constant. This gives, from eqs 5 and 6,

$$D_1 = \frac{L_{11}}{c_2 T} \left(\frac{\partial \mu_1}{\partial c_1}\right)_{T,P,c_2,D_1,D_2} = \frac{L_{11}}{c_2 T} \left(\frac{RT}{c_1}\right) = \frac{RL_{11}}{c_1 c_2} \quad (9)$$

and

$$\Gamma_1 = \frac{L_{11}}{c_2 T} \left(\frac{\partial \mu_1}{\partial D_1}\right)_{T,P,c_1,c_2,D_2} = \frac{L_{11}}{c_2 T} \left(\frac{RT}{D_1}\right) = \frac{RL_{11}}{c_2 D_1} = c_1 \quad (10)$$

where the last equality is due to eq 9. Therefore, eq 6 reduces to the revised Fick's law

$$\mathbf{j}_1 = -D_1 \nabla(c_1) - c_1 \nabla(D_1) = -\nabla(D_1 c_1) \quad (11)$$

This result demonstrates that the revised Fick's law formalism can indeed be approached from the more general perspective of nonequilibrium thermodynamics.

2. THE REVISED FOURIER'S LAW EQUATION IS NOT APPLICABLE TO SOLID SYSTEMS

Application of the revised Fourier's law equation for solid systems creates a violation of the second law of thermodynamics. In section 2.2 of our previous paper,¹ the heating of an electric wire with temperature-dependent thermal and electrical conductivities was analyzed as an example demonstrating how applying the revised Fourier's law equation affects calculations; this was not a proper example.

To explain this, let us consider a situation in which we have an isolated block of solid material that has a continuous and mild one-dimensional (1D) gradient of thermal conductivity, k (say, k increases with x , from left to right, as shown in Figure 1 below). The revised Fick's law ($q = -\frac{\partial(kT)}{\partial x}$) suggests that, at thermodynamic equilibrium ($q = 0$), the product kT must be constant throughout the volume of the material and therefore T should decrease with x . This result (a nonuniform distribution of temperature in an isolated solid) is a clear

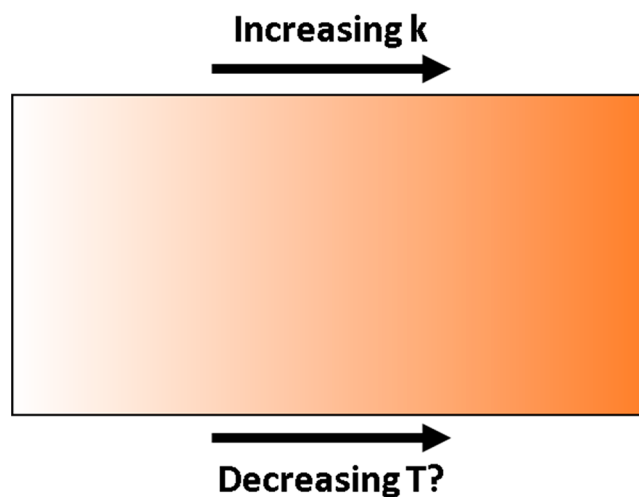


Figure 1. Isolated block of solid material with a continuous one-dimensional (1D) gradient of thermal conductivity, k .

violation of the second law of thermodynamics, as explained below.

Whether a gradient material that exists in a frozen chemically nonequilibrium (“glassy”) state can reach internal thermal equilibrium is a question. A uniform temperature distribution in a chemical gradient system at thermodynamic equilibrium can be mathematically proven as follows. Let us consider an isolated chemically inhomogeneous material in which the chemical composition is continuously varying in the x -direction; accordingly, the heat capacity also varies along the x -axis. The total entropy (S) and energy (U) of the material can be calculated, respectively, as

$$S[T(x)] = \rho A \int_0^L dx \int_{T_{\text{ref}}}^T \frac{\tilde{C}_v(x, T)}{T} dT \quad (12)$$

and

$$U[T(x)] = \rho A \int_0^L dx \int_{T_{\text{ref}}}^T \tilde{C}_v(x, T) dT \quad (13)$$

where $\tilde{C}_v(x, T)$ is the specific heat capacity, the density (ρ) and the cross-sectional area (A) of the material are assumed to be constant, and L is the length of the material along the x -direction. The equilibrium temperature profile ($T = f(x)$) that maximizes S under the constraint that U is constant (and is equal to U_0) can be determined using the method of Lagrange multipliers in functional space. It can be shown that the Euler–Lagrange equation for this problem reduces to

$$\frac{\tilde{C}_v(x, T)}{T(x)} - \lambda \tilde{C}_v(x, T) = 0 \quad (14)$$

where λ is an arbitrary constant (called the Lagrange multiplier); details will be given in a future paper. A rearrangement gives

$$T(x) = \frac{1}{\lambda} (\text{constant independent of } x) \quad (15)$$

This result proves that an isolated material having a gradient in chemical composition must also reach a state of uniform temperature at thermodynamic equilibrium; the temperature equalization is a direct mathematical consequence of applying

the principle of entropy maximization (the second law of thermodynamics) to an isolated system.

In the derivation of the revised Fourier's law (shown in Section 2.1 of our previous paper¹), the conductive heat flux (i.e., the molecular transport of the internal energy) was considered as occurring due to collision of the molecules, which is only applicable to liquids and gases. Then, it was deduced that the exact same argument can be applied to heat conduction in a solid body by replacing molecular transport with phonon transport. We concede that the latter step lacked a rigorous mathematical/theoretical underpinning, and therefore it is an unjustifiable stretch of reason to apply the revised Fourier's law equation to a solid system. The second term of the revised Fourier's law equation ($\mathbf{q} = -\nabla(kT) = -k\nabla T - T\nabla k$) is actually akin to the so-called Dufour effect (a heat flow due to a concentration gradient) that can only occur in fluids.²

We note that it remains a debate whether an isolated body of fluid in which compositional nonuniformity is spontaneously present (e.g., an isolated gas column in a gravitational field) must have uniform temperature at equilibrium; when convective mixing dominates over molecular diffusion, the temperature profile is no longer expected to be isothermal.⁸ As discussed in further detail in the Supporting Information (SI), in a gradient fluid there normally exists nondiffusive (convective) flow of molecules ($\mathbf{v} \neq 0$),⁴ and as a result, the effects of external body forces (such as the gravitational force) and also other mechanisms of contact energy transport (such as convective energy flux ($\mathbf{q}^{(c)}$) and work flux produced by pressure and viscous forces (\mathbf{w})) become operative.⁹ Even in a simplistic situation with negligible work due to external forces and negligible irreversibility associated with viscous dissipation that is subject to microscopic reversibility for energy transfer (i.e., even when the total energy flux is zero everywhere ($\mathbf{e} = \mathbf{q}^{(c)} + \mathbf{q} + \mathbf{w} = \mathbf{0}$)), \mathbf{q} does not have to be zero everywhere. Microscopic reversibility is a sufficient condition for equilibrium. Therefore, in an isolated gradient fluid at equilibrium, even if we assume that T is uniform ($\nabla T = 0$) throughout the space, thermal equilibrium does not require \mathbf{q} to be zero everywhere; in fact, in this case, \mathbf{q} is generally unlikely to be zero (because $\mathbf{q}^{(c)} + \mathbf{w}$ is unlikely to be zero), which is consistent (at least qualitatively) with what the revised Fourier's law equation suggests ($\mathbf{q} = -\nabla(kT) = -T\nabla k \neq 0$). Strictly speaking, for situations involving gradient fluids, the convective motions of the fluids bring analysis outside the domain of classical thermodynamics. A more rigorous investigation is warranted. At this point, our view is that the revised Fourier's law (which only concerns heat transfer by conduction (\mathbf{q})) does not produce any predictions that are inconsistent with the principle of internal thermal equilibrium (the second law of thermodynamics) or the principle of energy conservation (the first law of thermodynamics). A more detailed/rigorous version of this discussion is presented in the SI.

3. THE REVISED FOURIER'S LAW DOES NOT VIOLATE THE POSTULATE OF POSITIVE LOCAL ENTROPY PRODUCTION

It is a postulate of nonequilibrium thermodynamics that the entropy production is always positive everywhere, i.e., even for a microscopic control volume at any location in space. In the absence of mass and momentum transfer and chemical reactions, the entropy production rate per unit volume is given as^{2,3}

$$\sigma = -\frac{1}{T^2} \mathbf{q} \nabla T \geq 0 \quad (16)$$

Substitution of the revised Fourier's law equation ($\mathbf{q} = -\nabla(kT) = -k\nabla T - T\nabla k$) into eq 16 gives

$$\sigma = \frac{1}{T^2} (k\nabla T + T\nabla k) \nabla T \geq 0 \quad (17)$$

The first term on the left-hand side contains a perfect square ($(\nabla T)^2$), and is thus always positive. The thermal conductivities of liquids and gases typically increase with increasing temperature because of increased molecular collisions⁹ (i.e., $\nabla k \nabla T > 0$), which makes the second term always positive as well. Therefore, the revised Fourier's law would not create a situation that violates the premise of nonequilibrium thermodynamics. We note that as mentioned above this discussion is only relevant to situations which do not involve any mass or momentum transfer processes. However, as discussed in section 2, a gradient in k ($\nabla k \neq 0$) in a fluid system would normally create a convective flow of molecules, and in such circumstances, mass and momentum transfer effects would not be negligible; additional mass and momentum transfer terms are needed for calculation of σ in eq 16.³

4. OTHER MINOR POINTS

Below is the reiteration of the derivations of eqs 52 and 53 of our paper,¹ in which further explanations are given on the skipped steps. If we assume that the system obeys the principle of detailed balance (microscopic reversibility ($j_p = 0$ at all x) which is a sufficient condition for equilibrium), we obtain

$$v_e = \frac{1}{p_e} \left. \frac{\partial(pD)}{\partial x} \right|_e = \frac{1}{p_e} \left(p_e \left. \frac{\partial D}{\partial x} \right|_e + D_e \left. \frac{\partial p}{\partial x} \right|_e \right) \quad (18)$$

where v_e and p_e denote the convection velocity and probability density at equilibrium, respectively; here, the term "equilibrium" (the subscript "e") is used just for convenience, although, as discussed in the paper, "detailed balance" is not equivalent to "equilibrium." If we assume that v and D are independent of time, we obtain

$$v = \frac{1}{p_e} \left(p_e \frac{\partial D}{\partial x} + D \frac{\partial p}{\partial x} \right) = \frac{1}{p_e} \left(p_e \frac{\partial D}{\partial x} + D \frac{\partial p_e}{\partial x} \right) \quad (19)$$

Assuming that p_e is a weak function of x , we get

$$v \approx \frac{\partial D}{\partial x} \quad (20)$$

which is eq 52 of our paper.¹ Substitution of this equation into eq 47 gives eq 53 of the paper¹ as shown below.

$$\begin{aligned}\frac{\partial p}{\partial t} &\approx -\frac{\partial}{\partial x}\left(\frac{\partial D}{\partial x}p\right) + \frac{\partial^2}{\partial x^2}(Dp) \\ &= -p\frac{\partial^2 D}{\partial x^2} - \frac{\partial D}{\partial x}\frac{\partial p}{\partial x} + \frac{\partial}{\partial x}\left(p\frac{\partial D}{\partial x} + D\frac{\partial p}{\partial x}\right) \\ &= -p\frac{\partial^2 D}{\partial x^2} - \frac{\partial D}{\partial x}\frac{\partial p}{\partial x} + p\frac{\partial^2 D}{\partial x^2} + \frac{\partial D}{\partial x}\frac{\partial p}{\partial x} + \frac{\partial D}{\partial x}\frac{\partial p}{\partial x} \\ &\quad + D\frac{\partial^2 p}{\partial x^2} \\ &= \frac{\partial}{\partial x}\left(D\frac{\partial p}{\partial x}\right)\end{aligned}\quad (21)$$

Overall, we believe that our derivations of the revised Fick's, Fourier's, and Newton's law formulas are based upon sound reasoning and these equations are consistent with the established laws of physics. Implications of these ideas are profound. Further study is warranted.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.0c02856>.

Further detailed discussion supporting the argument that the revised Fourier's law does not violate the laws of thermodynamics (PDF)

■ ACKNOWLEDGMENTS

We are grateful for funding from NSF (CBET-1803968) and from ACS PRF (602033-ND7).

■ REFERENCES

- (1) Won, Y. Y.; Ramkrishna, D. Revised Formulation of Fick's, Fourier's, and Newton's Laws for Spatially Varying Linear Transport Coefficients. *ACS Omega* **2019**, *4*, 11215.
- (2) de Groot, S. R.; Mazur, P. *Non-Equilibrium Thermodynamics*; Dover Publications: New York, 1984.
- (3) Kondepudi, D.; Prigogine, I. *Modern Thermodynamics: From Heat Engines to Dissipative Structures*, 2nd ed.; Wiley & Sons: West Sussex, UK, 2015.
- (4) Dill, K. A.; Bromberg, S. *Molecular Driving Forces: Statistical Thermodynamics in Biology, Chemistry, Physics, and Nanoscience*, 2nd ed.; Garland Science: New York, 2010.
- (5) Porter, D. A.; Esterling, K. E.; Sherif, M. Y. *Phase Transformations in Metals and Alloys*, 3rd ed.; CRC Press, 2009.
- (6) Rosenfeld, Y. Relation between Transport Coefficients and Internal Entropy of Simple Systems. *Phys. Rev. A: At., Mol., Opt. Phys.* **1977**, *15*, 2545.
- (7) Won, Y. Y.; Lee, H. "pH Phoresis": A New Concept That Can Be Used for Improving Drug Delivery to Tumor Cells. *J. Controlled Release* **2013**, *170*, 396.
- (8) Verkley, W. T. M.; Gerkema, T. On Maximum Entropy Profiles. *J. Atmos. Sci.* **2004**, *61*, 931.
- (9) Bird, R. B.; Stewart, W. E.; Lightfoot, E. N.; Klingenberg, D. J. *Introductory Transport Phenomena*; John Wiley & Sons, 2015.