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Comment on "A Check of Prigogine's Theorem of Minimum Entropy Production in a Rod in a Nonequilibrium Stationary State"

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If the diffusivity varies in this linear fashion Eq. (4) may be written as

$$\frac{d^2C}{d\lambda^2}+2\lambda\frac{dC}{d\lambda}+k\left[C\frac{d^2C}{d\lambda^2}+\left(\frac{dC}{d\lambda}\right)^2\right]=0, \tag{A2}$$

where $\lambda=(y-h)/2\sqrt{D_0t}$ and C is the dimensionless solute concentration. The method of solution in Ref. 16 is to expand $C(\lambda)$ as a power series in k:

$$C(\lambda)=F_0(\lambda)+kF_1(\lambda)+k^2F_2(\lambda)+\cdots. \tag{A3}$$

Substituting Eq. (A3) and its derivatives into Eq. (A2) and demanding that the coefficient of each power of k separately vanishes, one obtains a set of differential equations for the F_i. To first order the solutions of these differential equations (F_i) and their derivatives ($dF_i/d\lambda$) are given by

$$F_0(\lambda)=\frac{C_0}{2}(1-\Phi(\lambda)), \tag{A4}$$

$$\frac{dF_0}{d\lambda}=-\frac{C_0}{2}\Phi_1(\lambda), \tag{A5}$$

$$F_1(\lambda)=\frac{C_0}{8}\left(1-\Phi^2-\frac{\Phi_1^2}{2}+\lambda\Phi_1-\lambda\Phi\Phi_1\right), \tag{A6}$$

$$\frac{dF_1}{d\lambda}=\frac{C_0\Phi_1}{8}[1-2\lambda^2-(3-2\lambda^2)\Phi+\lambda\Phi_1^2], \tag{A7}$$

where C_0 is the initial concentration, Φ is the error function, and $\Phi_1=d\Phi/d\lambda$. Since

$$\frac{dn}{dy}=\frac{dn}{dC}\frac{dC}{d\lambda}\frac{\partial\lambda}{\partial y}$$

we may use Eqs. (A3)–(A7) with Eq. (12) to express the theoretical refractive index gradient. The fitting to experiment is now performed by adjusting the parameters k and D_0. We performed this analysis for the case of the aqueous sucrose solution, setting $k=-0.32$ and $D_0=4.7\times10^{-6}$ cm^2/s, and achieved only a slightly better fit than that shown in Fig. 5. While these values are not in close agreement with the experimental values found in Ref. 14: $k=-0.23$ and $D_0=5.2\times10^{-6}$ cm^2/s, the fact that the variable diffusivity results are quite close to the constant diffusivity results establishes the main point of this analysis, namely, that a single, average diffusivity may in certain cases adequately model the behavior of a concentration-dependent diffusivity.

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Comment on ''A check of Prigogine's theorem of minimum entropy production in a rod in a nonequilibrium stationary state'' by Irena Danielewicz-Ferchmin and A. Ryszard Ferchmin [Am. J. Phys. 68 (10), 962–965 (2000)]

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In this article, the authors assert that the experimentally observed linear dependence of temperature on position in a rod whose ends are in contact with a hot and a cold thermal reservoir is a demonstration of Prigogine's theorem[1] of minimum entropy production. An implicit claim of the article is that there exists an established and verifiable principle of minimum entropy production, i.e., ''Prigogine's theorem,'' and the explicit claim is that this principle is verified by the experimental results presented in the article. Both of these claims are questionable. First, stationary states can be shown to correspond to minimum entropy production only when the Onsager coefficients are constant.[2] This is seldom the case in practice, and it is certainly not true in the case of heat conduction. Second, the data presented in the paper merely demonstrate that entropy production is a nonincreasing function of time. The observed linear dependence of temperature on position clearly does *not* correspond to minimum entropy production.

Following the authors, we consider a rod of length L, parallel to the x axis, with one end, at $x=0$, in contact with a hot reservoir at temperature T_h and the other end, at $x=L$, in contact with a cold reservoir at temperature T_c. The heat current is

$$\mathbf{J}=L_{qq}\nabla\left(\frac{1}{T(x)}\right), \tag{1}$$

where $T(x)$ is the temperature of the rod, $L_{qq}=\kappa T^2(x)$ is an Onsager coefficient, and κ is the temperature independent thermal conductivity. The entropy production per volume associated with heat flow can be written as the product of the generalized force $\nabla(1/T)$ and the conjugate flux $\mathbf{J}$; the entropy production per area is

$$P=\int_0^L \mathbf{J}\cdot\nabla\left(\frac{1}{T(x)}\right)dx=\int_0^L \frac{\kappa}{T^2(x)}\left(\frac{\partial T(x)}{\partial x}\right)^2 dx. \tag{2}$$

This expression is what the authors call the total entropy production in their paper.

It has been verified experimentally that Fourier's law holds, that is, that

$$\mathbf{J}=\kappa\nabla T(x). \tag{3}$$

In the steady state, $\nabla\cdot\mathbf{J}=0$ and it follows that

$$\frac{\partial^2 T(x)}{\partial x^2}=0. \tag{4}$$

The solution to Eq. (4), which satisfies Fourier's law, is

$$T_F(x)=T_h-(T_h-T_c)\frac{x}{L}, \tag{5}$$

in agreement with the authors' experimental observations.

The entropy production is an extremum when the first variation with respect to the temperature field vanishes, that is, when

$$\left(\frac{\partial T(x)}{\partial x}\right)^2=T(x)\frac{\partial^2 T(x)}{\partial x^2}. \tag{6}$$

This clearly differs from Eq. (4). The solution of Eq. (6), which minimizes entropy production, is

$$T_M(x)=T_h\exp\left(-\frac{x}{L}\ln\frac{T_h}{T_c}\right). \tag{7}$$

This exponential dependence of temperature on distance, to our knowledge, has not been observed.

The entropy production for the temperature field $T_F(x)$ which is observed is simply

$$P_F=\int_0^L \frac{\kappa}{T_F^2(x)}\left(\frac{\partial T_F(x)}{\partial x}\right)^2 dx=\frac{\kappa}{L}\left(\sqrt{\frac{T_h}{T_c}}-\sqrt{\frac{T_c}{T_h}}\right)^2, \tag{8}$$

while for the field $T_M(x)$ which minimizes entropy production it is

$$P_M=\int_0^L \frac{\kappa}{T_M^2(x)}\left(\frac{\partial T_M(x)}{\partial x}\right)^2 dx=\frac{\kappa}{L}\left(\ln\frac{T_h}{T_c}\right)^2. \tag{9}$$

It is straightforward to show that $P_F>P_M$ for all $T_h>T_c$.

In summary, the steady state observed by the authors (and by many others), in which the temperature varies linearly with distance, is *not* the state of minimum entropy production. The linear dependence of temperature on distance, which is in agreement with the well-established Fourier's law of heat conduction, in fact indicates that Prigogine's ''theorem'' of minimum entropy production, at least in the case of thermal conduction with temperature independent thermal conductivity, does *not* hold.

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