Using refractive index gradients to measure diffusivity between liquids

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One most commonly thinks of refraction occurring when light strikes at an angle to an interface separating two regions with different refractive indices. However, a light ray traveling normal to such an interface will also be refracted, if the second region has a refractive index gradient parallel to the interface plane. If liquid–liquid interdiffusion produces such a gradient in the second region, then one can infer the diffusivity of solute particles by measuring the time-dependent refraction. We have performed such diffusion experiments with three different aqueous solutions and found reasonably good agreement with diffusivity values given in the literature. The experimental setup and data analysis are simple enough for an undergraduate student to complete in a few weeks, making this investigation ideal for inclusion in an advanced laboratory course. © *2001 American Association of Physics Teachers*.
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I. INTRODUCTION

Twenty-five years ago Barnard and Ahlborn[1] published an article describing the deflection of a laser beam by a refractive index gradient. In their experiment the mixing in a vertical column between a pure liquid and a solution produced a refractive index gradient (dn/dy). As the solute particles diffused upward into the pure liquid, this gradient was generated by the varying solute concentration. By measuring the deflection produced in a horizontally incident laser beam, therefore directed perpendicular to the refractive index gradient, they determined this refractive index gradient as a function of vertical position. With the appropriate experimental conditions, the gradient was directly proportional to the angular deflection of the beam, enabling a straightforward measurement of the vertical variation of the gradient.

Since particle diffusion produced the variation in the solute concentration which in turn produced the refractive index gradient, their plot of the gradient versus vertical position $(dn/dy$ vs $y)$ changed over time. However, since the area under this curve is simply the difference in the index of refraction between the pure liquid and the initial solution, the area remained constant. Barnard and Ahlborn concluded their paper by noting that this technique ''can be used to follow the mixing of two liquids.'' Approximately two years after this possibility was noted, Bassi *et al.*[2] published a paper demonstrating the effectiveness of a sophisticated realization of this technique in making high precision measurements of liquid interdiffusivity. In this paper we present a simpler version of the technique, suitable for inclusion in an advanced undergraduate laboratory. Using classical diffusion theory, we have generated theoretical gradient profiles $(dn/dy$ vs $y)$ as a function of time. By fitting these to the experimental profiles we have determined the diffusion coefficient (D) for several types of solute molecules in water, finding reasonable to good agreement with values reported in the literature.

The reference literature cites a number of techniques to experimentally determine the diffusion coefficients in liquid solutions,[3] with interference-based optical methods being among the most precise and sensitive.[4] However, these interference methods, due to their relative complexity in experimental setup and analysis, may be considered problematic for inclusion in an advanced undergraduate laboratory curriculum in which a few weeks are allotted for a given experiment. The optical method described here is simple, low-cost, and may be completed by undergraduate students in a few weeks. Furthermore, its combination of concepts from optics, dielectric theory, and classical diffusion provides an interesting mixture of physical concepts, the sort of combination often encountered in scientific experimentation, but often lacking in much of a student's undergraduate education. A review of the last thirty years of *American Journal of Physics* and *The Physics Teacher* yields several articles reporting on the experimental investigation of diffusion in liquids. One group of articles describes the use of light scattering to measure the diffusivity of relatively large particles $(0.01–50 \ \mu m)$.[5,6] Here we report on the diffusion of much smaller particles (5–10 Å) where light scattering is negligible. For particles of this type we find two articles in the physics education literature: one using buoyancy as a method of determining solute concentration,[7] the other using a holographic technique.[8]

II. EXPERIMENTAL SETUP AND PROCEDURE

A schematic of the setup is shown in Fig. 1. A He–Ne laser is directed onto a glass cylinder whose axis is perpendicular to the beam and ~45° to the vertical, spreading the beam into a plane. The light travels ~1 m from the cylinder, striking a glass-walled cell (6.5 cm×6.5 cm×1.8 cm) containing the liquid. Since the beam is spread into a plane tilted ~45° to the vertical, the light strikes the cell at different heights which, having different refractive gradients, produce different angular deflections. The refracted light leaves the cell, traveling ~2 m before striking a screen. The 1 m distance from the cylindrical lens to the cell ensures that the light is nearly perpendicular to the vertical surface of the fluid, while the 2 m distance from the cell to the screen enables an accurate measurement of the small angle of deflection.

During the filling of the cell, it is important to minimize mixing so that an initial sharp boundary exists between the pure liquid and the solution. This can be accomplished by a simple method described in Ref. 8. To enable filling from below, a reservoir with a shut-off valve is connected by a
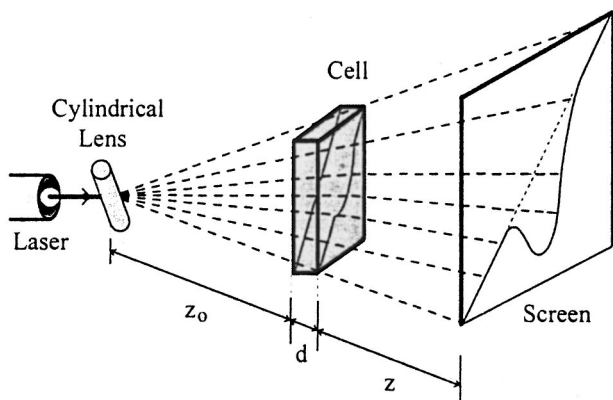
Fig. 1. Schematic of the geometry of the experimental setup: distance between cylindrical lens and cell $z_0 \sim 1$ m, cell thickness $d \sim 2$ cm, and distance between cell and screen $z \sim 2$ m. The thin diagonal lines in the cell are the laser trace upon entering the cell (straight line) and upon leaving the cell (refracted line).

tube to a small hole (~ 0.5 cm diameter) in the bottom of the cell housing. We fill the reservoir with the solution (greater density), allowing a complete filling of the tube until the liquid level is flush with the bottom of the cell. The cell is then filled halfway from above with the pure liquid (lesser density), and finally the shut-off valve is opened to allow the solution to slowly flow into the cell from below. We typically use 15–20 min for this final slow filling, which keeps the initial mixing layer thickness less than 2 mm.

Before filling the cell, the beam strikes the screen along a straight line at $\sim 45°$ to the vertical. After filling, the different angular deflections at different heights produce a curved laser trace on the screen. Figure 2 is a sketch of this curved trace made by the laser. At numerous locations we measure the vertical position of the undeflected trace (ξ) and the vertical deflected distance (δ) between this diagonal base line and the curved trace.

III. DETERMINATION OF THE EXPERIMENTAL GRADIENT OF THE REFRACTIVE INDEX

To obtain a profile of the refractive index gradient as a function of vertical position in the fluid we must connect the vertical position on the screen (ξ) to the vertical height in the
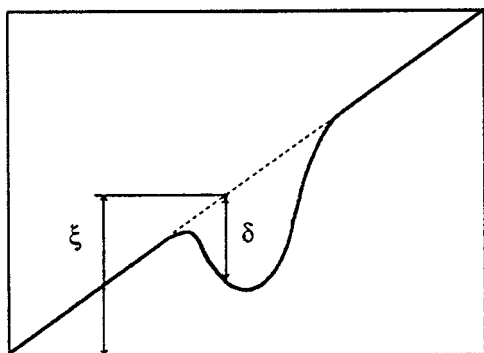

Fig. 2. Sketch of the curved laser trace appearing on the recording screen. Relative to the features shown, the actual laser trace is slightly wider than is depicted in this sketch. Direct measurements of the deflection (δ) and its associated vertical position (ξ) allow determination of the refractive gradient (dn/dy) at a given vertical position (y) in the diffusion cell.
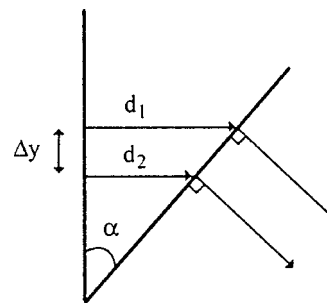

Fig. 3. Geometrical relationship between incident and refracted wave fronts using Huygens' construction. A vertical variation in the refractive index causes light rays separated by distance Δy to travel different distances in time Δt. This causes a new wave front to form at angle α with respect to the initial wave front.

cell (y), and connect the vertical deflection (δ) to the gradient (dn/dy). From the geometry of the experimental setup we have

$$ y = \frac{\xi z_0}{z_0 + d + z}, \tag{1} $$

where the various distances (z, z_0, d) are shown in Fig. 1. We develop the connection between δ and dn/dy using Huygens' principle. We restrict this analysis to the limiting case that the thickness of the cell (d) and the refractive index gradient are both small enough that the refracted angle (α) produces negligible vertical displacement of the ray within the cell. In this limit each ray travels at nearly constant vertical height within the cell and is deflected by a single refractive gradient associated with this height. Figure 3 shows a schematic of two light rays in this limit. The rays are separated by a vertical distance Δy traveling a time Δt through a medium with a refractive index gradient. Assuming the refractive index decreases with increasing height, the upper ray travels a distance $d_1 = (c/n)\Delta t$ while the lower ray travels a distance $d_2 = (c/(n+\Delta n))\Delta t$. A Huygens' construction of the refracted wave front produces the angular deflection shown in Fig. 3. By simple trigonometry we have

$$ \tan \alpha \approx \alpha \approx \left(\frac{c}{n}\Delta t\right)\left(\frac{\Delta n/\Delta y}{n}\right) \approx d\,\frac{dn/dy}{n}. \tag{2} $$

Reference 4 contains a more sophisticated analysis using the short wavelength limit of Maxwell's equations, the eikonal differential equation, which in the small angle limit reduces to Eq. (2). The ray undergoes an additional refraction as it leaves the cell producing a final angle of refraction in air (β) given by $n \sin \alpha \approx n\alpha \approx \sin \beta \approx \tan \beta$, where the index of air is taken to be one. Combining these results with the fact that $\tan \beta = \delta/z$ (see Fig. 1) one obtains

$$ \frac{dn}{dy} = \frac{\delta}{zd}. \tag{3} $$

IV. DETERMINATION OF THE THEORETICAL GRADIENT OF THE REFRACTIVE INDEX

For an interdiffusing two-component fluid, where the solute concentration (C) depends on vertical position and the index of refraction depends on the concentration, we may write the expected refractive index gradient as

$$dn/dy = \left(\frac{dn}{dC}\right)\left(\frac{dC}{dy}\right).$$

We use a Fick's law diffusion model to produce an expression for the time-dependent dC/dy and a simple dielectric model to create an expression for dn/dC. Fick's law states that the particle current density is proportional to the gradient of the particle concentration, where the proportionality constant is the diffusion coefficient, or diffusivity, D. Combining this with the continuity equation gives, in one dimension,

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial y}\left(D\frac{\partial C}{\partial y}\right). \tag{4}$$

Equation (4) has been written to allow for the possible variation of the diffusion coefficient with concentration: $D(C)$. If we assume that the diffusivity is independent of concentration the solution of Eq. (4) is straightforward. For an initial ''narrow spike'' of concentration C_0 the model predicts that the concentration will take a Gaussian shape with a width that spreads with time.[9] In our experimental situation, the initial concentration approaches a step function: $C=C_0(y\leq h)$, $C=0(y>h)$, where h is the initial height of the solution. For this case Fickian diffusion produces[10]

$$C(y,t) = \frac{C_0}{2}\left(1-\text{erf}\left(\frac{y-h}{2\sqrt{Dt}}\right)\right), \tag{5}$$

where erf(z) is the error function given by

$$\text{erf}(z) = \frac{2}{\sqrt{\pi}}\int_0^z \exp(-s^2)ds. \tag{6}$$

This solution [Eq. (5)] assumes an infinitely long fluid column, so that diffusing particles never reflect from a boundary. For a finite-sized column with particle reflection at the ends the solution becomes[11]

$$C(y,t) = \frac{C_0}{2}\sum_{k=-\infty}^{\infty}\left[\text{erf}\left(\frac{h+2kL-y}{2\sqrt{Dt}}\right)+\text{erf}\left(\frac{h-2kL+y}{2\sqrt{Dt}}\right)\right], \tag{7}$$

where L is the total height of the two-component fluid column. Differentiating this expression yields

$$\frac{dC}{dy} = \frac{C_0}{2\sqrt{\pi Dt}}\sum_{k=-\infty}^{\infty}\left\{\exp\left[-\left(\frac{h+2kL+y}{2\sqrt{Dt}}\right)^2\right]\right.$$
$$\left.-\exp\left[-\left(\frac{h+2kL-y}{2\sqrt{Dt}}\right)^2\right]\right\}. \tag{8}$$

Given our experimental parameters: $h\cong 3$ cm, $L\cong 6$ cm, $D\sim 5\times 10^{-6}$ cm^2/s, only a small fraction of diffusing particles $(0.01C_0)$ approach the boundaries after ~ 38 h. Since the time duration of our experiments has never exceeded this duration, we have found that limiting the summation in Eq. (8) to $|k|\leq 2$ is more than sufficient to account for any particle reflection.

For a material, the index of refraction arises from the dipole moment per unit volume ($\mathbf{P}$) taken to be linearly dependent on the average electric field: $\mathbf{P}=\chi\varepsilon_0\mathbf{E}$, where χ is the volume electric susceptibility of the material. The phase velocity of an electromagnetic wave is $\nu=\sqrt{1/\varepsilon\mu_0}=c/n$ where
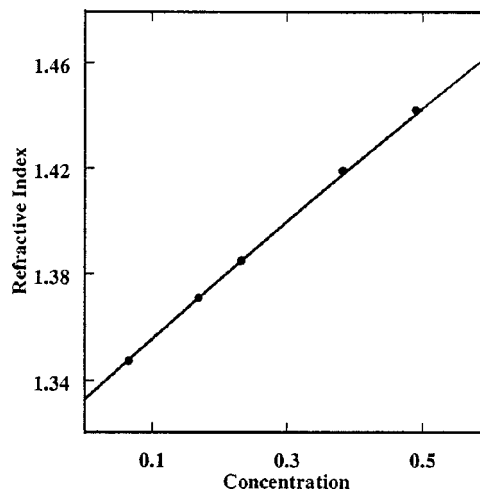

Fig. 4. Comparison of experimental ($\bullet$) and theoretical ($-$) refractive indexes as a function of sucrose concentration in water. Experimental values are measured with an Abbé refractometer and theoretical values are calculated from Eq. (11) with $n_s=1.545$ and $n_f=1.333$.

c is the velocity in vacuum and $\varepsilon=(1+\chi)\varepsilon_0$. Combining these last two equations we may express the susceptibility as

$$\chi = n^2+1. \tag{9}$$

Solute and solvent molecules in a solution will contribute distinct electric susceptibilities given by χ_s and χ_f, respectively. If the fractional volume of the solute in the solution is F, then the susceptibility of the solution is given by

$$\chi = F\chi_s+(1-F)\chi_f. \tag{10}$$

We can express the concentration C as a dimensionless, relative solute concentration defined as the ratio of the number of solute particles per unit volume in solution to the number of solute particles per unit volume in the pure solute. Using the fact that C equals F and using Eq. (9), we may rewrite Eq. (10) as

$$n^2 = n_f^2+C(n_s^2-n_f^2). \tag{11}$$

This form of the refractive index's dependence on concentration may be experimentally tested using an Abbe refractometer. Figure 4 shows the theoretical prediction of Eq. (11) for sucrose in water to be in good agreement with the measured values. Fits of similar quality were also obtained for the two other solutions investigated: glycerol in water and sodium thiosulfate in water. Differentiating Eq. (11) we obtain

$$\frac{dn}{dC} = \frac{n_s^2-n_f^2}{2\sqrt{n_f^2+C(n_s^2-n_f^2)}}. \tag{12}$$

Multiplying Eq. (8) by Eq. (12) produces the theoretical expression for dn/dy.

V. RESULTS AND DISCUSSION

By adjusting the diffusion coefficient (D) we have successfully modeled the time-dependent experimental gradient curves [Eq. (3)] for three aqueous solutions. Figure 5 shows results for a sodium thiosulfate solution using $D=7.5\times 10^{-6}$ cm^2/s, while Fig. 6 shows results for a sucrose solution using ($D=4.0\times 10^{-6}$ cm^2/s). A similar quality of agree-
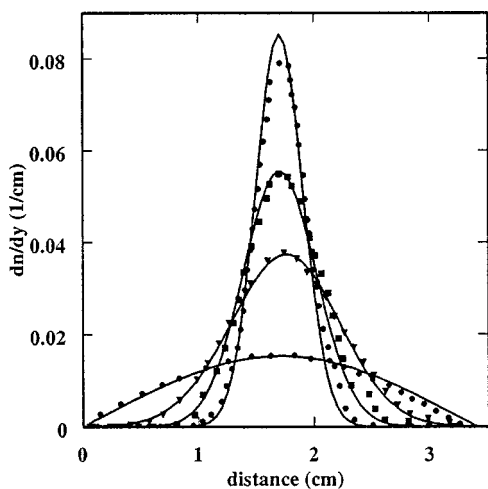
Fig. 5. Comparison of experimental and theoretical refractive index gradients for sodium thiosulfate in water at different times. Symbols are the experimental results at the following times: (●) 46 min, (■) 109 m, (▼) 241 m, (●) 1387 m. The solid line is a theoretical prediction with $D = 7.5 \times 10^{-6}$ cm^2/s. Initial concentration is 0.27 g/ml.

ment between theory and experiment is achieved for a glycerol solution ($D = 6.0 \times 10^{-6}$ cm^2/s). Since the diffusivity controls the time dependence of the height and width of the theoretical curves, a 10%–20% change in D produces a significant degradation in the fit to experiment. In both Figs. 5 and 6 we have omitted curves for times when the mixing region has a width of less than ~1.5 cm, since the large refractive gradient produces a large angle of deflection, which violates the small angle approximation we assume in theory.

As in the case with aqueous sodium thiosulfate, students in an advanced lab setting may wish to work with a solute/solvent combination whose D value is unknown. In these cases an order of magnitude estimate of the expected diffusivity is instructive. The Stokes–Einstein relation provides such an estimate by considering the case of a sphere of ra-

dius R diffusing through a fluid with viscosity η. In this idealized situation we may estimate the diffusion coefficient to be

$$D = \frac{k_B T}{6 \pi \eta R}. \tag{13}$$

For low concentration solutions this expression yields reasonably accurate results for molecules whose masses are less than several hundred atomic mass units,[12] while for higher concentrations, such as used in the present work, we expect only qualitative agreement with experiment.[13] Using the viscosity of water, the temperature (293 K), and experimental diffusion coefficient ($D = 7.5 \times 10^{-6}$ cm^2/s), Eq. (13) yields a quite reasonable effective molecular radius of ≈ 3 Å for sodium thiosulfate.

Unlike sodium thiosulfate, the diffusivities of aqueous solutions of sucrose[14] and glycerol[15] have been measured over a range of concentrations. Based on the Stokes–Einstein relation, if not physical intuition, we expect the diffusivity to decrease as the viscosity increases with increasing concentration. This is indeed the case for sucrose and glycerol; furthermore this decrease is nearly linear with increasing concentration for both solutes over the concentration range present in our experiment (see Refs. 14 and 15). Based on these results, we estimate the average diffusivity appropriate for our experiment to be that for a concentration equal to 50% of our initial concentration. According to Refs. 14 and 15, our expected average diffusivities are 4.4×10^{-6} cm^2/s for sucrose and 7.1×10^{-6} cm^2/s for glycerol.

While these diffusivity values are reasonably close to those we obtained, one might question the validity of replacing a concentration-dependent diffusivity with a single average diffusivity. In the Appendix we present an approximate solution of Eq. (4) assuming a linear dependence of diffusivity on concentration. We have not included this discussion in the main body of this paper since we feel the mathematical complexity introduced in the analysis undercuts one purpose of this paper, which is to introduce a simple method of analyzing the diffusion process in liquids. Furthermore, this more sophisticated analysis produces theoretical results which are nearly indistinguishable from those found using a single, average diffusivity.

In conclusion, we have presented a simple experimental technique whereby one may determine the diffusion coefficient of solute particles in a liquid. The results are in reasonable agreement with those obtained using more sophisticated techniques. The technique is well suited for inclusion in an advanced undergraduate lab course, with the analysis requiring a nice combination of topics drawn from optics, dielectric theory, and classical diffusion theory.

ACKNOWLEDGMENTS

APPENDIX

In this Appendix we use the work of J. Gillis and O. Kedem[16] to construct an approximate solution to Eq. (4) assuming that the diffusion coefficient varies according to

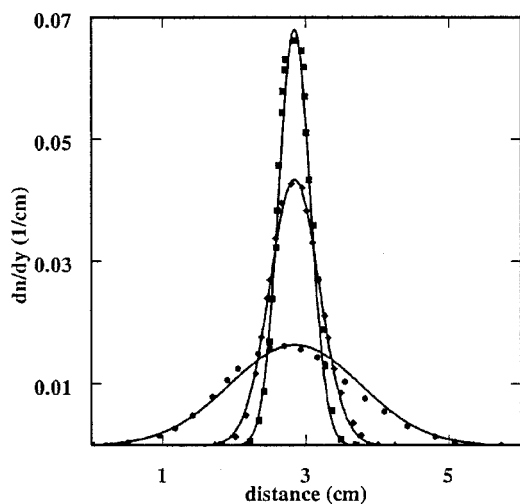$$D = D_0 (1 + kC). \tag{A1}$$

Fig. 6. Comparison of experimental and theoretical refractive index gradients for sucrose in water at different times. Symbols are the experimental results at the following times: (■) 100 min, (♦) 245 m, (●) 1736 m. The solid line is the theoretical prediction with $D = 4.0 \times 10^{-6}$ cm^2/s. The initial concentration of sucrose is 0.30 g/ml.

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

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

where $\lambda = (y-h)/2\sqrt{D_0 t}$ 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:

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

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

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

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

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

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

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 $D_0 = 4.7$

$\times 10^{-6}$ 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 $D_0 = 5.2 \times 10^{-6}$ 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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