Relative stability in nonuniform temperature

by N. G. van Kampen

Landauer has suggested that the relative stability of a particle diffusing in a bistable potential is affected by an intervening hot layer. We derive this effect both from thermodynamics and from the diffusion equation. For this purpose the proper form of the diffusion equation in a nonuniform medium is established for the case of a Brownian particle. If the diffusion takes place in a ring, the hot layer creates a steady current.

1. Introduction

Consider the diffusion of a particle in one dimension in the presence of an external force $V(x)$. First suppose that the medium is homogeneous and isothermal, so that the mobility μ and the diffusion coefficient D do not depend on x. Then the probability density $P(x, t)$ of the particle obeys the familiar diffusion or Smoluchowski equation,

$$\frac{\partial P(x, t)}{\partial t} = \mu \frac{\partial}{\partial x} V'(x)P(x, t) + D\frac{\partial^2 P(x, t)}{\partial x^2}. \qquad (1)$$

This equation, or its equivalent Langevin version, has been used to model a large variety of physical situations.

The stationary solution is easily found to be

$$P^s(x) = C\exp\left[-\frac{V(x)}{D}\right],$$

$$C^{-1} = \int \exp\left[-\frac{V(x)}{D}\right] dx.$$

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The integral exists when $V(x)$ increases sufficiently rapidly for $x \to \pm\infty$, which we shall assume. In order that P^s be identical with the thermal equilibrium distribution P^e, one must have the fluctuation-dissipation, or Einstein, relation

$$D = T_0\mu \qquad \text{(Boltzmann's constant = 1).} \qquad (2)$$

T_0 is the temperature of the heat bath (e.g., the phonons), which is responsible for the diffusion.

Suppose $V(x)$ is bistable, as in **Figure 1**, so that P^e consists of two peaks concentrated near points a and c. We want the peaks to be clearly separated, and therefore suppose that the energy barrier is large: $W/T_0 \gg 1$. It is then possible to take the integral over each peak separately:

$$\pi_a^e = C\int_{-\infty}^{b} e^{-V(x)/T_0}dx,$$

$$\pi_c^e = C\int_{b}^{\infty} e^{-V(x)/T_0}dx.$$

These are the probabilities for the particle to be in either well. As the boundary between the peaks I have chosen the point b where V is maximal; this is of course somewhat arbitrary, but any point not too far from b gives the same values up to a correction of relative order $\exp[W/T_0]$. It should be borne in mind that the quantities π_a^e, π_c^e have physical meaning only with this margin of precision. Their ratio has been called the relative stability of the two states a and c.

For many years Rolf Landauer has been telling us that a localized inhomogeneity in the temperature between these two maxima will alter their relative stability [1, 2]. Specifically, he supposed that in some interval (x_1, x_2) confined to the slope of the potential between a and b (**Figure 2**), the temperature is raised to $T_1 > T_0$. His idea was that this has the effect of pumping particles from a into c, so that in the stationary nonequilibrium state one has $\pi_a^s < \pi_a^e$, $\pi_c^s > \pi_c^e$.

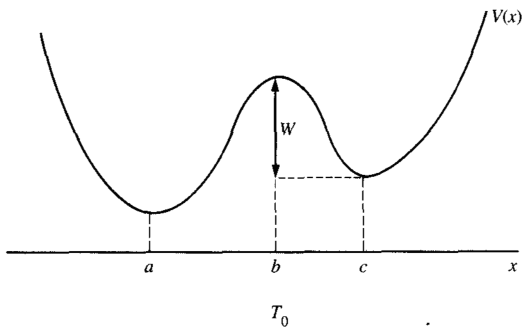

Figure 1

Particle with energy $V(x)$ interacting with an isothermal bath at T_0.

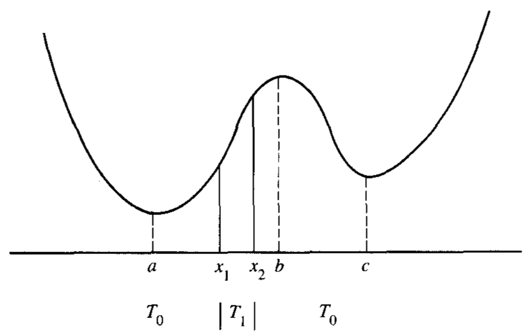

Figure 2

Particle with energy $V(x)$; in the interval (x_1, x_2) the bath temperature is at T_1.

Landauer's words went unheeded until recently both M. Büttiker and I happened to look more closely at his idea. In Section 2 I give a phenomenological derivation of the effect, based on thermodynamics. A more mathematical derivation, based on the diffusion equation, is given in Section 3. It is of course necessary to modify Equation (1), since it can no longer be true that both μ and D are independent of x; see Equation (2). The question of how to write the diffusion equation if the medium is not homogeneous has been the subject of some debate in semiconductor physics [2, 3–5]. There does not seem to be a universal answer; rather, the correct form of the equation depends on the physical system considered. For our present purpose it is sufficient to consider a very simple model, which is specified in Section 4. It leads to the following equation for diffusion in a one-dimensional inhomogeneous medium whose temperature depends on x:

$$\frac{\partial P(x, t)}{\partial t} = \frac{\partial}{\partial x} \mu(x) \left[V'(x)P(x, t) + \frac{\partial}{\partial x} T(x)P(x, t) \right]. \qquad (3)$$

In anticipation of this derivation in Section 4, we use Equation (3) as our starting point in Section 3. It should be remarked, however, that the phenomenon we are studying occurs anyway, regardless of the precise form of the diffusion equation.

An interesting modification is obtained when the diffusion takes place in a ring. Then the pumping effect of the hot region in the presence of an external potential gives rise to a steady current. This is also computed in Section 3.

2. Thermodynamics

First consider the isothermal case of Figure 1. The particle interacts with a heat bath T_0, and the total energy E_0 of the particle plus bath is constant. If the particle is at some position x, it has the energy $V(x)$, so that the energy of the bath is $E_0 - V(x)$. Thus the entropy of the bath is

$$S_0[E_0 - V(x)] = S_0(E_0) - \frac{dS_0}{dE_0} V(x) = S_0(E_0) - \frac{V(x)}{T_0}.$$

The probability for this to happen is therefore

$$P^e(x) = Ce^{-V(x)/T_0}. \qquad (4)$$

This is the familiar derivation of the canonical distribution. The particle itself has the single degree of freedom x, so that it has no entropy and its phase space is measured by dx; hence, Equation (4) is actually its probability density in x-space.

Now let the temperature in an interval (x_1, x_2) be raised to T_1, as in **Figure 2**. That means that there is a second heat bath T_1 with which the particle interacts whenever it is in this interval. If the particle enters at x_1 and leaves at x_2, it has picked up the energy $V(x_2) - V(x_1)$ from the second heat bath. Hence, the entropy of this heat bath T_1 has decreased by the amount

$$-\frac{V(x_2) - V(x_1)}{T_1}.$$

On the other hand, the heat bath T_0 has gained the same amount of energy, so that its entropy has increased by

$$\frac{V(x_2) - V(x_1)}{T_0}.$$

Thus, the passage of the particle through the interval (x_1, x_2) has the effect of transferring the energy $V(x_2) - V(x_1)$ from the hot bath to the colder one and thereby increasing the entropy of the total system by the amount

$$\{V(x_2) - V(x_1)\} \left(\frac{1}{T_0} - \frac{1}{T_1} \right).$$

The exponential of this entropy increase is the factor by which the probability for the particle to be on the right of x_2 is enhanced. Hence, in the nonisothermal stationary situation one has

$$\frac{\pi_c^s}{\pi_a^s} = \frac{\pi_c^e}{\pi_a^e} \exp\left[\{V(x_2) - V(x_1)\}\left(\frac{1}{T_0} - \frac{1}{T_1}\right)\right].$$

This is the Landauer effect.

It is possible to obtain a more explicit expression for the relative stability. For this purpose we approximate in the usual way the curve $V(x)$ near its minima by parabolas and find

$$\pi_a^e = C \int \exp\left[-\frac{1}{T_0}\{V(a) + \tfrac{1}{2}(x-a)^2 V''(a)\}\right] dx$$

$$= C\sqrt{\frac{2\pi T_0}{V''(a)}}\, e^{-V(a)/T_0},$$

$$\pi_c^e = C\sqrt{\frac{2\pi T_0}{V''(c)}}\, e^{-V(c)/T_0}.$$

Hence

$$\frac{\pi_c^s}{\pi_a^s} = \sqrt{\frac{V''(a)}{V''(c)}}$$

$$\cdot \exp\left[-\frac{V(c) - V(x_2)}{T_0} - \frac{V(x_2) - V(x_1)}{T_1} - \frac{V(x_1) - V(a)}{T_0}\right]. \quad (5)$$

The square root in this expression represents the ratio of the widths of both wells. The exponential may be written

$$\exp\left[-\int_a^c \frac{V'(x)}{T(x)}\, dx\right] = \exp\left[-\int_a^c \frac{dV}{T}\right]. \quad (6)$$

In this form it can be applied to general temperature profiles $T(x)$.

3. Solution of the diffusion equation

This section is based on the diffusion equation (3), which is derived in the next section. In the stationary case the probability flow must vanish:

$$\mu(x)\left[V'(x)P^s(x) + \frac{d}{dx}\, T(x)P^s(x)\right] = 0.$$

Hence

$$P^s(x) = \frac{B}{T(x)} \exp\left[-\int_{-\infty}^{x} \frac{V'(x')}{T(x')}\, dx'\right], \quad (7)$$

so that

$$\frac{P^s(c)}{P^s(a)} = \frac{T(a)}{T(c)} \exp\left[-\int_a^c \frac{V'(x)}{T(x)}\, dx\right].$$

The exponent is the same as in Equation (6), so that we again find the pumping effect. The factor T^{-1} in front of the exponential in Equation (7) is discussed in Section 5.

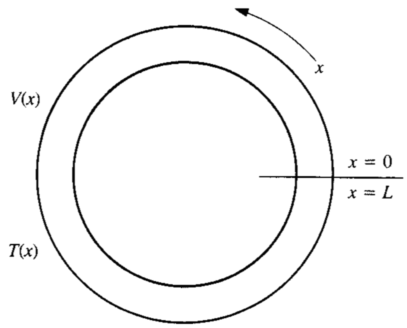

Figure 3

Diffusion in a ring with energy $V(x)$ and temperature distribution $T(x)$ along the ring.

An interesting possibility is an arrangement in which the particles, having been pumped into c, can diffuse back into a along an alternative route that bypasses the hot zone. To put it differently, consider diffusion in a ring, with a potential $V(x)$ along the ring and a varying temperature $T(x)$; see **Figure 3**. We now have to find the stationary solution of Equation (3) in an interval $0 < x < L$ with periodic boundary conditions

$$P(0) = P(L), \qquad \left.\frac{dP}{dx}\right|_0 = \left.\frac{dP}{dx}\right|_L,$$

where L is the length of the ring. The condition for stationarity is in this case that the flow is a constant J, independent of x:

$$-\mu(x)\left[V'(x)P^s(x) + \frac{d}{dx}\, T(x)P^s(x)\right] = J.$$

Incidentally, this stationarity condition implies trivially that the flow is periodic in x, so that the second boundary condition need no longer be taken into account.

The equation can readily be solved. With the abbreviation

$$\int_0^x \frac{V'(x')}{T(x')}\, dx' = \Phi(x),$$

one finds

$$P^s(x) = \frac{e^{-\Phi(x)}}{T(x)}\left[T(x)P^s(0) - J\int_0^x \frac{dx'}{\mu(x')}\, e^{\Phi(x')}\right].$$

The two integration constants J and $P^s(0)$ are determined by the remaining boundary condition and by the normalization requirement. The former gives

$$[e^{\Phi(L)} - 1]T(0)P^s(0) = -J\int_0^L \frac{dx'}{\mu(x')}\, e^{\Phi(x')}. \quad (8)$$

One sees that the flow vanishes when $\Phi(L) = 0$, that is, when the integral of dV/T around the ring vanishes. In fact, in that case no net change of entropy occurs when the particle goes around.

The normalization condition is

$$1 = T(x)P^s(x) \int_0^L \frac{dx}{T(x)} e^{-\Phi(x)} - J \int_0^L \frac{dx}{T(x)} e^{-\Phi(x)} \int_0^x \frac{dx'}{\mu(x')} e^{\Phi(x')}.$$

Combination with Equation (8) yields, after some algebra, the explicit value of the flow:

$$J = -\frac{e^{\Phi(L)} - 1}{\displaystyle\int_0^L \int_0^L \frac{dx}{T(x)} \frac{dx'}{\mu(x')} e^{\Phi(x')-\Phi(x)}[1 + \Theta(x - x')\{e^{\Phi(L)} - 1\}]}.$$

Θ is the Heaviside step function. This is hardly a transparent result, but it does show that for given μ, T, and V a uniquely determined flow occurs.

4. Derivation of Equation (3)

Our model for diffusion in an inhomogeneous, nonisothermal medium is a Brownian particle governed by Kramers' equation for the joint distribution of position and velocity [6],

$$\frac{\partial R(x, v, t)}{\partial t} = -v \frac{\partial R}{\partial x} + V'(x) \frac{\partial R}{\partial v} + \gamma(x) \frac{\partial}{\partial v}\left[vR + T(x) \frac{\partial R}{\partial v}\right]. \tag{9}$$

In the case of constant damping γ and temperature T, it is well known [6, 7] how to derive from it, in the limit of large γ, a diffusion equation for the spatial distribution $P(x) = \int R(x, v)dv$. All we have to do now is to adapt this derivation to the present case. Actually, it is a straightforward application of the systematic method for eliminating fast variables [8], but for the present purpose I do not invoke the general formalism.

Because γ is large, the lowest approximation $R^{(0)}$ must satisfy

$$\frac{\partial}{\partial v}\left[vR^{(0)} + T \frac{\partial R^{(0)}}{\partial v}\right] = 0.$$

Leaving aside solutions that do not vanish fast enough for $|v| \to \infty$, one obtains

$$R^{(0)}(x, v, t) = e^{-v^2/2T} f(x, t), \tag{10}$$

with arbitrary f. The next order in $1/\gamma$ must obey

$$\frac{\partial R^{(0)}}{\partial t} + v\frac{\partial R^{(0)}}{\partial x} - V'(x)\frac{\partial R^{(0)}}{\partial v} = \gamma\frac{\partial}{\partial v}\left[vR^{(1)} + T\frac{\partial R^{(1)}}{\partial v}\right]. \tag{11}$$

Integration over v annihilates the right-hand member; hence one obtains as an integrability condition that the integral over the left-hand member must be zero. On substituting Equation (10) one finds that this condition amounts to $\partial f/\partial t = 0$.

Subsequently one has to solve $R^{(1)}$ from Equation (11):

$$e^{-v^2/2T}\left[vf' + \frac{v^2}{2T^2} T'f + \frac{v}{T} V'f\right] = \gamma T \frac{\partial}{\partial v} e^{-v^2/2T} \frac{\partial}{\partial v} e^{v^2/2T} R^{(1)}.$$

As an *ansatz* set,

$$R^{(1)}(x, v, t) = [v\phi(x, t) + v^3\psi(x, t)]e^{-v^2/2T}.$$

The equation is satisfied if ϕ and ψ are taken to be

$$\psi = -\frac{T'}{6\gamma T^2} f, \qquad \phi = -\frac{(Tf)' + V'f}{\gamma T}.$$

They are independent of t. The general $R^{(1)}$ is obtained by adding an arbitrary solution of the homogeneous equation:

$$R^{(1)} = [v\phi(x) + v^3\psi(x) + g(x, t)]e^{-v^2/2T}.$$

The equation for the next approximation $R^{(2)}$ again yields an integrability condition

$$\int dv\left[\frac{\partial R^{(1)}}{\partial t} + v\frac{\partial R^{(1)}}{\partial x} - V' \frac{\partial R^{(1)}}{\partial v}\right] = 0.$$

This equation can be written

$$\begin{aligned}
\frac{\partial}{\partial t} \int R^{(1)}dv &= -\frac{\partial}{\partial x} \int vR^{(1)}(x, v)dv \\
&= -\frac{\partial}{\partial x} \int [v^2\phi(x) + v^4\psi(x)]e^{-v^2/2T}dv \\
&= -\frac{\partial}{\partial x} \sqrt{2\pi T}\,[T\phi(x) + 3T^2\psi(x)] \\
&= -\sqrt{2\pi}\, \frac{\partial}{\partial x} \frac{1}{\gamma}\left[\frac{\partial}{\partial x} T^{3/2}f + V'T^{1/2}f\right].
\end{aligned}$$

At this point we return to the spatial distribution in order to collect the results:

$$\begin{aligned}
P(x, t) &= \int R^{(0)}(x, v)dv + \int R^{(1)}(x, v, t)dv + \cdots \\
&= \sqrt{2\pi T} f(x) + O(1/\gamma).
\end{aligned}$$

The equation obtained for $R^{(1)}$ can be translated into

$$\frac{\partial P}{\partial t} = \frac{\partial}{\partial x} \frac{1}{\gamma}\left[\frac{\partial}{\partial x}TP + V'P\right] + O(\gamma^{-2}).$$

This is the desired equation (3); the mobility $\mu(x)$ is to be identified with the reciprocal of the damping coefficient $\gamma(x)$.

5. Discussion

The diffusion term (3), which we derived for the Brownian particle, has neither the form

$$\frac{\partial}{\partial x} D(x) \frac{\partial}{\partial x} P(x, t) \quad \text{nor} \quad \frac{\partial^2}{\partial x^2} D(x)P(x, t),$$

which were the subject of the debate [2–5]. The three forms under consideration do not differ in their coefficients of the second derivative of P, but they differ by terms involving the first derivative. These terms are of the same type as what is loosely called the drift term. Thus Equation (3) may be written equivalently as

$$\frac{\partial P}{\partial t} = \frac{\partial}{\partial x}(\mu V' + \mu T')P + \frac{\partial}{\partial x} D \frac{\partial P}{\partial x}, \tag{12}$$

or as

$$\frac{\partial P}{\partial t} = \frac{\partial}{\partial x}(\mu V' - \mu' T)P + \frac{\partial^2}{\partial x^2} DP. \tag{13}$$

In neither case does the drift term have the form of mobility times force. In Equation (12) one might perhaps interpret the drift term by saying that V has to be supplemented by an additional "thermal potential" T, but that seems rather contrived. In Equation (13) not even such a contrived interpretation is possible. One cannot, of course, tamper with the definition of the mobility μ without violating Equation (2).

The fact that in Equation (3) the factor T comes after the derivative gave rise to the factor T^{-1} in the stationary solution (7). This factor exhibits the Soret effect and can roughly be explained as follows. In a region of high temperature, the particle moves more rapidly than in a lower temperature. Hence, taken over a very long time, it spends on the average less time in the hotter regions than would appear from phase-space considerations alone. This explains the appearance of a temperature-dependent factor in the stationary distribution. This explanation does not specify the precise form of that factor, however, for which the actual calculation is needed. Similar considerations led Landauer [2] to expect in another model the factor $T^{-1/2}$. As these factors are not related to the phase space, they cannot be found from a thermodynamic argument such as the one in Section 2.

Finally, we try to understand the additional drift terms from a heuristic point of view. Suppose that at some time t the particle is at some point x. At $t + \Delta t$ it will be at $x + \Delta x$, where Δx is a random quantity. One sees immediately from Equation (13) that for small Δt

$$\frac{\langle \Delta x \rangle}{\Delta t} = -\mu(x)V'(x) + \mu'(x)T(x),$$

$$\frac{\langle (\Delta x)^2 \rangle}{\Delta t} = 2D(x) = 2\mu(x)T(x).$$

The latter equation is the familiar one, and in the former the term $-\mu V'$ is also familiar. The unexpected addition $\mu' T$ to the drift can be explained as follows. To arrive at Equations (13) or (3), we have taken in Equation (9) the limit $\gamma \to \infty$. That implies that during Δt the particle undergoes many changes of velocity, and Δx is the outcome of many small random steps. During these steps the particle samples the neighborhood of x and thereby feels the variation of μ in that neighborhood; hence the factor $\mu'(x)$. The size of the steps is governed by the heat motion; hence the factor T. A more detailed discussion will be given elsewhere.

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