

Brownian motion, the second law and Boltzmann

Trevor W Marshall

36, Victoria Avenue, Didsbury, Manchester M20 8RA, England

Received 20 July 1982, in final form 17 September 1982

Abstract The relative merits of ‘Boltzmann entropy’ and ‘Gibbs entropy’ are discussed. It is found that, for describing the irreversible features of Brownian motion, the ‘Gibbs entropy’ is the superior concept. In terms of this we see that Brownian motion gives an excellent illustration of the second law of thermodynamics.

The historical origins of the ‘Gibbs entropy’ are examined, and it is concluded that Ludwig Boltzmann must be given a substantial part of the credit for it. On the other hand, the equation $S = k \log W$, which has been attributed posthumously to Boltzmann, does less than full justice to his concept of entropy, and has led to serious misunderstandings in the theory of Brownian motion.

Résumé On discute des mérites relatifs de ‘l’entropie de Boltzmann’ et de ‘l’entropie de Gibbs’. Il apparaît que ‘l’entropie de Gibbs’ est un concept mieux adapté à la description des aspects d’irréversibilité liés au mouvement brownien. Le mouvement brownien, dans ce contexte, assure alors une excellente illustration du Second Principe.

Les origines historiques de ‘l’entropie de Gibbs’ sont examinées, et l’on montre que Boltzmann a joué un rôle important dans l’introduction de ce concept. D’un autre côté, l’équation $S = k \log W$, qui a fait l’objet d’une attribution posthume à Boltzmann, ne rend que très imparfaitement justice à sa vision de l’entropie, et a conduit à des malentendus graves dans la théorie du mouvement brownien.

1. Introduction

The problem of deriving the laws of irreversible heat flow from the reversible dynamics of molecules is as old as Newton’s dynamics itself. It is certainly much older than either Fourier’s heat conduction equation or Carnot’s statement of the second law of thermodynamics (Brush 1976a). However, the modern formulation of the problem dates from Clausius’s discovery of the entropy, and subsequent efforts by Boltzmann to express the entropy as a microscopic state function.

Boltzmann’s attack on this problem has been divided into three phases (Brush 1976b, Klein 1973, Kuhn 1978b).

The first phase was initiated by his article (Brush, 1966) of 1872, where he defined a function E (later to be called H):

$$E(t) = \int f(\mathbf{u}, t) \log f(\mathbf{u}, t) d^3\mathbf{u} \quad (1.1)$$

$Nf d^3\mathbf{u}$ being the number of molecules which have velocities in a rectangular cell of velocity space between \mathbf{u} and $\mathbf{u} + d\mathbf{u}$. He constructed the transport equation for f (the famous Boltzmann equation)

and deduced that, provided f satisfies a certain initial condition, the function E (or H) decreases monotonically with t . The initial condition has become known as the Stosszahlansatz (ter Haar 1954). Boltzmann claimed to have derived his transport equation directly from Newtonian dynamics, so his description of the time evolution may be properly described as deterministic. Any system satisfying the initial Stosszahlansatz must necessarily show monotonic behaviour of the H function. He proposed that the entropy was equal to this function multiplied by a negative constant.

The second phase was stimulated by a criticism of Boltzmann’s H theorem from his colleague Loschmidt. This criticism has become known as the Umkehrwand (ter Haar 1954), and it arises from the observation that, if, at a some time, t , in the evolution of an N molecule system, the velocities of all molecules are reversed, then, between t and $2t$, the system reverses its original evolution arriving back at its initial state. During this time interval the H function *increases* monotonically.

Boltzmann (1877) replied to this criticism by pointing out that, immediately after a collision, the

two colliding molecules have a degree of correlation in their velocities. After the reversal, this correlation is between molecules which are about to collide. Such a microscopic state does not satisfy the Stosszahlansatz. Therefore, Boltzmann argued, there must be some reason, arising from the dynamics, for such a 'turnabout' state to occur very rarely in actual N molecule systems. Such a state, though not altogether impossible, must be extremely improbable. He was able to show that the H function, and hence the entropy also, were proportional to the logarithm of a quantity, P , called the 'permutability' of the state. He characterised P as the number of microstates corresponding to the distribution f , and claimed that distributions with larger P were 'more probable' than those with smaller P . This led him to a conclusion already suggested by Maxwell: systems with finite N (that is, all physically realisable systems) evolve from lower to higher values of the entropy, S , with a probability close to one, but not with absolute certainty. His new 'probability' calculus enabled him to estimate this divergence from unity, and he found, even for such a small system as a cubic millimetre of gas, that it was so small as to give no detectable divergence from the second law.

The crowning achievement of this second phase was the statement that entropy is proportional to the logarithm of P . However, in his 'Lectures on Gas Theory' (Boltzmann 1964b), originally published in 1896, he referred to P as 'probability' and changed its designation to W (the first letter of 'Wahrscheinlichkeit'). His successors, therefore, felt it appropriate to inscribe the equation

$$S = k \log W \quad (1.2)$$

on his monument in the Zentralfriedhof of Vienna.

Naturally, no single equation can do justice to Boltzmann's creative genius. In the present article we shall see that, on the contrary, a preoccupation with this equation by Boltzmann's immediate successors has given rise to a serious misunderstanding in the theory of Brownian motion. This is something of a tragedy. The approach of a system of Brownian particles from an arbitrary initial distribution to its equilibrium distribution gives an excellent simple illustration of irreversible behaviour derived from a dynamical model. Many details of this behaviour were obtained by Boltzmann's pupil Smoluchowski (1916a), but he did not establish the connection with Boltzmann's H theorem. This is because the prevailing view, at the time he wrote and ever since (Brush 1976c), was that a Brownian particle is 'too small' to be treated as a thermodynamic system.

We shall see that this view is, in fact, mistaken. A single Brownian particle, like a single gas molecule, does not constitute a thermodynamic system. But a large assembly of such particles, like a large assembly of gas molecules, does constitute a ther-

modynamic system. It is possible to define an entropy function for this system, but because the bombarding molecules constitute a constant-temperature heat bath, it is the free energy, rather than the entropy, which exhibits monotonic behaviour.

Instead of the 'Boltzmann entropy' defined in equation (1.2), it will turn out that the entropy function giving this monotonic behaviour is more akin to the 'Gibbs entropy'. Smoluchowski specifically rejected Gibbs' entropy, because he thought it was constant in time. It is a cruel irony that, if he had only substituted his own probability distribution into the Gibbs entropy, he would have found that it is not constant, but, on the contrary, displays time evolution in accordance with the second law.

I will argue that the failure of Boltzmann's successors to arrive at this simple result, and of subsequent students of Brownian motion to extend it to the results of the present article, arises from a consistent neglect of Boltzmann's third phase. This began with his visit to the British Association meeting at Oxford in 1894, a meeting which he described as 'unforgettable' (Boltzmann 1964a). The central new idea was given the name of 'molecular disorder', but, to emphasise its novelty, I will prefer, in this article, to call it 'molecular disordering'. The disordering of a thermodynamic system arises because of a continual interaction with its environment, and results in a continual reimposition of the initial Stosszahlansatz. For a general system, the only known way to treat such an interaction is with the rather abstract tool of the Gibbsian canonical ensemble, but the system of Brownian particles is perhaps unique in that the 'environment' of bombarding molecules is quite accurately described by the stochastic force term in the Langevin equation. This produces a continual coarse-graining of the distribution, and is therefore exactly what is required in order to produce a non-constant Gibbs entropy (ter Haar 1954).

The recognition by Boltzmann (1895) that no thermodynamic system is closed, and that there is always a residual interaction with the environment, took him a very long way indeed from his determinist position of 1872. In the final section of this article, I will indicate how some of the conclusions he reached in the first two phases should have been modified in the light of his third phase. I shall also attempt to explain why such a task has been neglected by physicists in the present century.

2. Brownian motion in the strong-damping limit

We will now prove the assertion, made in the previous section, that an H theorem results from combining Smoluchowski's theory of Brownian motion with a Gibbs-type entropy.

The underlying dynamical equation for a particle of mass m performing one-dimensional motion in a

potential $V(x)$ is the Langevin equation (Chandrasekhar 1943):

$$m\ddot{x} + m\beta\dot{x} + V'(x) = E(t) \quad (2.1)$$

where the stochastic force, $E(t)$, is a gaussian white-noise with autocorrelation

$$K(\tau) = \langle E(t)E(t+\tau) \rangle = 2m\beta kT\delta(\tau). \quad (2.2)$$

If β is sufficiently large, we have the strong-damping limit, in which the inertia term may be neglected, so that the Langevin equation becomes

$$\dot{x} = \frac{1}{m\beta} [E(t) - V'(x)]. \quad (2.3)$$

Then the probability density, $W(x, t)$, satisfies the diffusion equation:

$$\frac{\partial W}{\partial t} = \frac{1}{m\beta} \frac{\partial}{\partial x} \left[kT \frac{\partial W}{\partial x} + V'(x)W \right]. \quad (2.4)$$

This equation was obtained by Smoluchowski (1916a), who also gave the boundary condition to be satisfied at a reflecting barrier, namely

$$kT \frac{\partial W}{\partial x} + V'(x)W = 0 \quad (2.5)$$

at $x = x_1$ (say). Consider now such a particle with reflecting barriers at x_1 and x_2 , so that it is constrained to move only in the interval $x_1 \leq x \leq x_2$. We define the entropy as

$$S(t) = -k \int_{x_1}^{x_2} W(x, t) \log W(x, t) dx. \quad (2.6)$$

Then the average energy is

$$U(t) = \int_{x_1}^{x_2} W(x, t) V(x) dx \quad (2.7)$$

and the free energy is

$$F(t) = \int_{x_1}^{x_2} W(V + kT \log W) dx \quad (2.8)$$

so

$$\dot{F} = \int_{x_1}^{x_2} \frac{\partial W}{\partial t} (V + kT \log W) dx. \quad (2.9)$$

We now substitute for $\partial W/\partial t$ and integrate by parts, making use of the boundary conditions, to obtain

$$\dot{F} = -\frac{1}{m\beta} \int_{x_1}^{x_2} \frac{1}{W} \left(kT \frac{\partial W}{\partial x} + V'W \right)^2 dx. \quad (2.10)$$

Since the integrand is everywhere non-negative, we have proved that

$$\dot{F} \leq 0. \quad (2.11)$$

Hence F decreases monotonically until, for large t , W satisfies, for all x , the equation

$$kT \frac{\partial W}{\partial x} + V'W = 0 \quad (2.12)$$

that is

$$W = c \exp(-V(x)/kT). \quad (2.13)$$

The theorem we have just proved is well illustrated by taking the case of an unrestricted particle in a harmonic potential, that is

$$V(x) = \frac{1}{2}m\omega^2 x^2 \quad (2.14)$$

where

$$x_1 = -\infty \\ x_2 = +\infty.$$

This boundary value problem may be solved in terms of the fundamental solution, for which the initial density is a delta function:

$$W(x, 0) = \delta(x - y). \quad (2.15)$$

The solution is then (Uhlenbeck and Ornstein 1930b)

$$W(x, t) = \frac{1}{\sigma\sqrt{(2\pi)^{\frac{1}{2}}}} \exp\left(-\frac{[x - y \exp(-\gamma t)]^2}{2\sigma^2}\right) \quad (2.16)$$

where

$$\sigma^2 = \frac{kT}{m\omega^2} [1 - \exp(-2\gamma t)] \quad (2.17)$$

and

$$\gamma = \frac{\omega^2}{\beta}.$$

The general solution is the convolution of equation (2.16) with an arbitrary initial distribution. Suppose, for example, that the initial distribution is gaussian:

$$W(x, 0) = \frac{1}{\sigma_0\sqrt{(2\pi)^{\frac{1}{2}}}} \exp\left(-\frac{(x - y)^2}{2\sigma_0^2}\right). \quad (2.18)$$

Then $W(x, t)$ is again given by equation (2.16), but the variance is now

$$\sigma^2 = \sigma_0^2 \exp(-2\gamma t) + \frac{kT}{m\omega^2} [1 - \exp(-2\gamma t)]. \quad (2.19)$$

With this distribution, the entropy is

$$S = \frac{1}{2}k[\log(2\pi\sigma^2) + 1] \quad (2.20)$$

and the energy is

$$U = \frac{1}{2}m\omega^2[\sigma^2 + y^2 \exp(-2\gamma t)]. \quad (2.21)$$

From equations (2.19) and (2.20), it follows that the entropy may either decrease or increase monotonically, depending on whether σ_0^2 is greater or less than $kT/m\omega^2$. But the rate of change of the

free energy is

$$\dot{F} = -\gamma m \omega^2 \exp(-2\gamma t) \left(y^2 + \frac{1}{\sigma^2} (\sigma^2 - kT/m\omega^2)^2 \right) \tag{2.22}$$

which is non-positive for all values of y and σ_0 .

3. Brownian motion in phase space

The entropy in equation (2.6) is of gibbsian type because, unlike equation (1.2), it is defined over the ensemble of possible positions. It is therefore not a function of x , the particle's instantaneous position. This was precisely Smoluchowski's reason (Smoluchowski 1916b) for preferring 'the customary Boltzmann entropy' to 'the Gibbs entropy, and one purpose of the present article is to show that his choice was an incorrect one.

But, generally speaking, Gibb's entropy is taken to be an integral over phase space, that is over N position and N momentum variables. For the case of Brownian particles this integral readily reduces to one, over single position and momentum variables, since the motion of the separate particles is assumed to be independent.

We should, therefore, be treating a probability density which is a function of position and velocity—for present purposes we need not distinguish between linear velocity and momentum. It is, of course, a limitation of Brownian motion in the strong-damping approximation that the velocity is not defined, which is why the equilibrium distribution (equation (2.13)) is a function only of the potential and not of the kinetic energy.

Subsequent to the pioneering work of Einstein and Smoluchowski, the theory of Brownian motion was extended to phase space by Uhlenbeck and Ornstein (1930a) and by Kramers (1940a). If we retain the inertia term in equation (2.1), then the probability density, $W(x, u, t)$, satisfies the equation

$$\frac{\partial W}{\partial t} = \frac{\partial}{\partial u} \left(\frac{\beta kT}{m} \frac{\partial W}{\partial u} + \beta u W + \frac{V'(x)}{m} W \right) - u \frac{\partial W}{\partial x}. \tag{3.1}$$

Kramers showed that, for suitably large values of β , the time-scales for establishing the Boltzmann distribution in position and velocity have two different orders of magnitude. For example, if we take the harmonic potential

$$V = \frac{1}{2} m \omega^2 x^2 \tag{3.2}$$

then the fundamental solution of equation (3.1), obtained from an initial density

$$W(x, u, 0) = \delta(x - y) \delta(u - v) \tag{3.3}$$

is

$$W(x, u, t) = \frac{1}{2\pi\Delta^{\frac{1}{2}}} \exp\left(-\frac{A}{2\Delta} (x - \bar{x})^2 + \right.$$

$$\left. + \frac{H}{\Delta} (x - \bar{x})(u - \bar{u}) - \frac{B}{2\Delta} (u - \bar{u})^2 \right). \tag{3.4}$$

Here (\bar{x}, \bar{u}) are the position and velocity which the particle would have in the absence of the stochastic force, and (Wang and Uhlenbeck 1945b)

$$A = \frac{2\beta kT}{m} \int_0^t \left(\frac{\mu_1 \exp(\mu_1 t') - \mu_2 \exp(\mu_2 t')}{\mu_1 - \mu_2} \right)^2 dt' \tag{3.5}$$

$$B = \frac{2\beta kT}{m} \int_0^t \left(\frac{\exp(\mu_1 t') - \exp(\mu_2 t')}{\mu_1 - \mu_2} \right)^2 dt' \tag{3.6}$$

$$H = \frac{\beta kT}{m} \left(\frac{\exp(\mu_1 t) - \exp(\mu_2 t)}{\mu_1 - \mu_2} \right)^2 = \frac{1}{2} \dot{B} \tag{3.7}$$

$$\Delta = AB - H^2 \tag{3.8}$$

where μ_1, μ_2 are the roots of

$$\mu^2 + \beta\mu + \omega^2 = 0. \tag{3.9}$$

For $\beta \gg \omega$, the two time scales are γ^{-1} are β^{-1} for the position and velocity respectively, where γ is defined by equation (2.17). Indeed, for values of t large compared with β^{-1} we find that

$$\bar{x} = y \exp(-\gamma t) \quad \bar{u} = 0 \tag{3.10}$$

and

$$A \approx \frac{kT}{m}$$

$$B \approx \frac{kT}{m\omega^2} [1 - \exp(-2\gamma t)] \tag{3.11}$$

$$H = 0.$$

It follows that, after an initial time of order β^{-1} , the phase space density is the simple product of Maxwell's velocity density and Smoluchowski's position density.

We now show that this two-stage approach to the Boltzmann distribution, like the single-stage approach of the previous section, is in conformity with the second law of thermodynamics. Indeed, since the proof is independent of the magnitude of β , we shall generalise the result of the previous section to Brownian motions in which the strong-damping approximation does not necessarily apply.

We define entropy and energy as follows:

$$S = -k \int_{x_1}^{x_2} dx \int_{-\infty}^{\infty} du W(x, u, t) \log W(x, u, t) \tag{3.12}$$

$$U = \int_{x_1}^{x_2} dx \int_{-\infty}^{\infty} du W(x, u, t) [\frac{1}{2} m u^2 + V(x)]. \tag{3.13}$$

Then

$$\dot{F} = \iint \frac{\partial W}{\partial t} (\frac{1}{2} m u^2 + V + kT \log W) dx du. \tag{3.14}$$

Let us now rewrite equation (3.1) as

$$\frac{\partial W}{\partial t} + \text{div } \mathbf{J} = 0 \tag{3.15}$$

where \mathbf{J} is a current vector in phase space,

$$\mathbf{J} = \left(uW, -\beta uW - \frac{V'}{m} W - \frac{\beta kT}{m} \frac{\partial W}{\partial u} \right). \quad (3.16)$$

Then, using the divergence theorem

$$\begin{aligned} \dot{F} &= \iint \mathbf{J} \cdot \text{grad} \left(\frac{1}{2} mu^2 + V + kT \log W \right) dx du \\ &\quad - \int \mathbf{J} \left(\frac{1}{2} mu^2 + V + kT \log W \right) \cdot \mathbf{n} dS. \end{aligned} \quad (3.17)$$

The integrand of the first term may be written as

$$-\frac{m\beta}{W} \left(uW + \frac{kT}{m} \frac{\partial W}{\partial u} \right)^2 + kT \left(u \frac{\partial W}{\partial x} - \frac{V'}{m} \frac{\partial W}{\partial u} \right). \quad (3.18)$$

Hence, using the divergence theorem again

$$\begin{aligned} \dot{F} &= -m\beta \iint \frac{1}{W} \left(uW + \frac{kT}{m} \frac{\partial W}{\partial u} \right)^2 dx du \\ &\quad + \int \mathbf{n} \cdot [kT\mathbf{J}' - (\frac{1}{2} mu^2 + V + kT \log W)\mathbf{J}] dS \end{aligned} \quad (3.19)$$

where

$$\mathbf{J}' = \left(uW, -\frac{V'}{m} W \right).$$

For any but the most pathological distributions, we may safely assume that the surface integrals over $u = \pm\infty$ are zero throughout the motion. The surface terms therefore reduce to $I(x_2) - I(x_1)$, where

$$I(x) = \int_{-\infty}^{\infty} uW(kT - \frac{1}{2} mu^2 - V - kT \log W) du. \quad (3.20)$$

There has been virtually no discussion in the literature of the boundary conditions, at x_1 and x_2 , which are appropriate in this case. Wang and Uhlenbeck (1945a) 'felt sure' that the condition

$$W(x, u, t) = W(x, -u, t) \quad (3.21)$$

must be satisfied for $x = x_1$ and $x = x_2$. We postpone discussion of this condition until the end of this section, and assume, for the moment, that it is satisfied. In that case $I(x_1)$ and $I(x_2)$ are both zero. Hence, from equation (3.19), we see that \dot{F} is again non-positive, which establishes the monotonic property of F .

Again this result is well illustrated by the unrestricted harmonic oscillator. If the initial distribution is gaussian, the calculation leading to equations (3.5), (3.6) and (3.7) is easily generalised to give

$$\begin{aligned} A &= \frac{kT}{m} + a\mu_1^2 \exp(2\mu_1 t) + b\mu_2^2 \exp(2\mu_2 t) \\ &\quad - 2h\mu_1\mu_2 \exp[(\mu_1 + \mu_2)t] \end{aligned} \quad (3.22)$$

$$\begin{aligned} B &= \frac{kT}{m\omega^2} + a \exp(2\mu_1 t) + b \exp(2\mu_2 t) \\ &\quad - 2h \exp(\mu_1 + \mu_2)t \end{aligned} \quad (3.23)$$

$$\begin{aligned} H &= a\mu_1 \exp(2\mu_1 t) + b\mu_2 \exp(2\mu_2 t) \\ &\quad - h(\mu_1 + \mu_2) \exp(\mu_1 + \mu_2)t \end{aligned} \quad (3.24)$$

where a , b and h are constants related to the initial covariances. The following relations may now be verified:

$$\dot{A} + \omega^2 \dot{B} = 2\beta \left(\frac{kT}{m} - A \right) \quad (3.25)$$

$$\dot{A} + 2\beta\Delta = \frac{2\beta kT}{m} B. \quad (3.26)$$

With the density given by equation (3.4), the energy and entropy are

$$U = \frac{1}{2} m(\bar{u}^2 + A) + \frac{1}{2} m\omega^2(\bar{x}^2 + B) \quad (3.27)$$

$$S = k[\log(2\pi\Delta^{1/2}) + 1]. \quad (3.28)$$

It follows that

$$\dot{F} = -\beta m\bar{u}^2 + \frac{1}{2} m(\dot{A} + \omega^2 \dot{B}) - kT\dot{\Delta}/2\Delta. \quad (3.29)$$

Substituting from equations (3.25) and (3.26), we obtain

$$\dot{F} = -\beta m\bar{u}^2 + 2\beta kT - \beta mA - \frac{\beta k^2 T^2 B}{m\Delta}. \quad (3.30)$$

It becomes evident that this is negative definite, if we use the identity

$$A \frac{m^2 \Delta^2}{k^2 T^2} + B\Delta - \frac{2m\Delta^2}{kT} = \mathbf{x}' \mathbf{A} \mathbf{x} \quad (3.31)$$

where

$$\mathbf{x}' = \left(B - \frac{m\Delta}{kT}, H \right)$$

and \mathbf{A} is the positive definite covariance matrix

$$\mathbf{A} = \begin{pmatrix} A & -H \\ -H & B \end{pmatrix}. \quad (3.32)$$

So the monotonic character of F is clearly displayed. On the other hand, S , far from being monotonic, can be made to have either a maximum or a minimum, for some finite value of t , by suitable choice of the initial covariance matrix.

Returning now to the boundary condition (3.21), it may be derived from the assumption that all collisions of the Brownian particle at a reflecting wall are elastic. For from this it follows that

$$\lim_{t \rightarrow t+} W(x_1, u, t') = \lim_{t \rightarrow t-} W(x_1, -u, t') \quad (3.33)$$

for $u > 0$, and

$$\lim_{t' \rightarrow t+} W(x_2, u, t') = \lim_{t' \rightarrow t-} W(x_2, -u, t') \quad (3.34)$$

for $u < 0$. Since we have already assumed W to be a differentiable, and hence continuous, function of x and t , equation (3.21) now follows.

It is, of course, desirable to extend the results of this section to Brownian motions with inelastic wall collisions, but that would be a vast extension beyond the scope of the present article. True, the strong-damping model of the previous section has a boundary condition (2.5) which expresses nothing more than particle conservation, but that is at the cost of ignoring the particle's velocity altogether. As noted in another context (Boyer 1969, Marshall 1981), Brownian motions of this more general kind will not even have the Boltzmann equilibrium distribution.

4. Brownian motion in the weak-damping limit

If β is small compared to the natural frequencies of the undamped system, it is again possible to deduce a one-dimensional diffusion equation (Kramers 1940b, Marshall 1980). The appropriate variable is now the action,

$$\xi = \frac{1}{2\pi} \oint mu \, dx. \quad (4.1)$$

Then the probability density, $W(\xi, t)$, satisfies the equation

$$\frac{\partial W}{\partial t} = \beta \frac{\partial}{\partial \xi} \left(\frac{kT\xi}{\omega} \frac{\partial W}{\partial \xi} + \xi W \right) \quad (4.2)$$

where

$$\omega(\xi) = \frac{dH}{d\xi} \quad (4.3)$$

and H is the energy

$$H = \frac{1}{2}mu^2 + V(x). \quad (4.4)$$

(Note that, in this case, collisions at all reflecting walls must be elastic in order that ξ be well defined.) For boundary values of ξ , there is only one boundary condition (Feller 1952) which gives a norm-preserving solution for W , namely

$$\frac{kT\xi}{\omega} \frac{\partial W}{\partial \xi} + \xi W = 0 \quad (4.5)$$

(at $\xi = \xi_1$ and ξ_2 , say). Now we define the energy and entropy as

$$U = \int_{\xi_1}^{\xi_2} H(\xi) W(\xi, t) \, d\xi \quad (4.6)$$

$$S = -k \int_{\xi_1}^{\xi_2} W(\xi, t) \log W(\xi, t) \, d\xi. \quad (4.7)$$

Then, following the usual partial integration procedure,

$$\dot{F} = -\beta \int_{\xi_1}^{\xi_2} \frac{\xi}{\omega W} \left(kT \frac{\partial W}{\partial \xi} + \omega W \right)^2 \, d\xi. \quad (4.8)$$

Provided the potential, $V(x)$, is such as to guarantee a closed orbit in phase space, ξ_1 and ξ_2 are non-negative, and also $\omega(\xi)$ is positive for all ξ between ξ_1 and ξ_2 . Hence F decreases monotonically to a limiting value for which

$$kT \frac{dW}{d\xi} + \omega W = 0 \quad (4.9)$$

that is

$$W = C \exp(-H/kT). \quad (4.10)$$

I do not know of any general method for solving equation (4.2) with boundary conditions (4.5). For a general potential the functional relationship between ω and ξ in equation (4.3) may be quite complicated. However a family of potentials with the relation

$$\xi = CH^{\alpha+1} \quad (\xi_1 = 0, \xi_2 = \infty) \quad (4.11)$$

has been treated by the same method used by Uhlenbeck and Ornstein (1930b) (Marshall 1982). A tedious, but straightforward calculation on the solutions of this family again shows that, while F decreases monotonically, S may reach its equilibrium value from either direction, depending on the initial value of ξ_0 . Note that the above family includes at least three simple potentials.

(i) The harmonic oscillator, with $V(x) = \frac{1}{2}m\omega^2 x^2$, has

$$\xi = \frac{H}{\omega}$$

so

$$\alpha = 0.$$

(ii) The free particle between reflecting walls, with

$$V(x) = \begin{cases} 0 & (0 < x < a) \\ \infty & (\text{otherwise}) \end{cases}$$

has

$$\xi = \left(\frac{2ma}{\pi^2} \right)^{1/2} H^{1/2}$$

so

$$\alpha = -\frac{1}{2}$$

(iii) The gravitating particle with a reflecting base, with

$$V(x) = \begin{cases} mgx & (x > 0) \\ \infty & (x \leq 0) \end{cases}$$

has

$$\xi = \left(\frac{8}{9m\pi^2 g^2} \right)^{1/2} H^{3/2}$$

so

$$\alpha = \frac{1}{2}.$$

5. Irreversibility and the growth of entropy

The main thrust of Ludwig Boltzmann's scientific work was devoted to finding a microscopic (or 'atomist') explanation of thermodynamic irreversibility. The tools which he fashioned for this task were, above all, the transport equation, which bears his name, and the H theorem. During his lifetime, these constituted what his colleagues would have considered 'the method of Boltzmann' (Kuhn 1978a), and we can safely assume that a monument erected in 1906, the year of his death, would have carried an inscription something like equation (1.1).

The formula, $S = k \log W$, was chosen as Boltzmann's epitaph at a time (1933) when the classical mechanics on which his transport equation was based had been triumphantly superseded by the new quantum mechanics. It may well have seemed natural then to draw attention to that aspect of his work which anticipated the new mechanics. Uhlenbeck (1927) has even suggested that Boltzmann had a 'premonition'(!) of the discrete division of phase space into cells of finite volume in quantum mechanics.

It does not seem to me fruitful to speculate on what attitude Boltzmann would have taken to the new mechanics. Rather, we should ask what light the posthumous formula throws on the central problem of irreversibility.

As we saw in §1, the recognition that entropy is related to probability came to Boltzmann as a result of his attempt to deal with Loschmidt's Umkehrinwand. By his division of phase space into cells he was able to derive a relation between the quantity used in his H theorem and another quantity called, at that time, the 'permutability' of the state. This quantity was subsequently termed (by Boltzmann) either 'relative probability' or just 'probability' and (by Planck) 'thermodynamic probability'. In his 'Popular Writings' (Boltzmann 1974), he was especially fond of the formulation that dynamical systems evolve with time from states of lower towards states of higher probability.

In this article we have seen, by a study of perhaps the simplest of all irreversible microscopic systems, that such a formulation is incorrect. Of course, it is frequently stated that only large dynamical systems go from lower to higher probability, and that a Brownian particle is 'too small' to be regarded as a thermodynamic system (Brush 1976c). Indeed, Einstein's famous inversion of the 'Boltzmann' equation to obtain

$$W = \exp(S/k) \quad (5.1)$$

is nowadays considered to be the foundation of the theory of fluctuations and Brownian motion was historically the first test of that theory.

On another occasion, however, Einstein emphasised the essentially *irreversible* aspect of Brownian motion. In a letter to Besso (Einstein and Besso 1979) he distinguished between a ciné film of a single Brownian particle and a ciné film of a cloud of such particles. In the latter, the tendency to diffusion is quite evident. In §2, §3 and §4 we showed how, by a correct definition of the entropy, it is possible to see Brownian motion as a vindication, rather than a violation, of the second law of thermodynamics. Also the correct time-variation of the entropy is a clear consequence of the stochastic force in the Langevin equation.

I would say that, while there may be some hints in Boltzmann's earlier writings that all thermodynamic systems, even 'isolated' ones, have some interaction with their environment, it was not until his 'Nature' article that such interactions were recognised as the basis of thermodynamic irreversibility. In §8 of his 'Lectures on Gas Theory', he recognised how much the new concept of 'molecular disordering' owed to the British kinetic theorists whom he met at the British Association meeting in 1894.

What neither Boltzmann nor his successors seem to have recognised is that such a view of the origin of irreversibility is radically different from that which he had when he first proved his H theorem. A continuous process of molecular disordering is very different from an initial Stosszahlansatz followed by a deterministic time evolution. Boltzmann's 1877 statement that, under such a time evolution, the permutability (or 'probability') increases monotonically, has never been given a satisfactory proof.

I submit that if, in 1877, Boltzmann had understood molecular disordering the way he did in 1895, he would have given a very different, and far better, reply to Loschmidt's criticism. Instead of trying to show that a state of the gas in which all molecules have their velocities reversed is improbable, he would have pointed out that, in order for the system to go back to its initial state, all the fields expressing the system's interaction with its environment would also have to be reversed. In modern parlance, it is the statistical independence of these fields from the particles' degrees of freedom which causes the dynamical system to lose its memory. So the time-reversal would be no more than a momentary hiccup of the system. It would resume its entropy-increasing evolution immediately after the reversal.

Only one short formal step is required for such a new analysis, namely the replacement of f by W in formula (1.1). At the same time it is necessary to insist that W is a true probability density, that is that its integral over the state space is one. This means abandoning the ill-understood notions of 'relative probability' and 'thermodynamic probability'. Above all it means abandoning $S = k \log W$.

Historians may argue about the degree of explicitness with which Ludwig Boltzmann made some of these steps. What can safely be said is that he gave us all the clues we needed to make them. He therefore, effectively, achieved his foremost scientific aim of deriving thermodynamic irreversibility from a microscopic model. I submit that that is more of an achievement than having a premonition of quantum mechanics.

Acknowledgment

An earlier version of this paper was presented at the International Conference on Ludwig Boltzmann at the University of Vienna in September 1981. I take this opportunity of thanking the organisers and the participants of that conference, whose discussions helped me to develop some of my ideas. The technical part of the work reported here was carried out during my employment as a lecturer in mathematics at the University of Manchester.

References

- Boltzmann L 1877 *Wiener Berichte* **76** 373
 — 1895 *Nature* **51** 413–5
 — 1964a *Lectures on Gas Theory* (Engl. transl.) University of California) p 22
 — 1964b *Lectures on Gas Theory* (Engl. transl.) University of California) §8
 — 1974 *Theoretical Physics and Philosophical Problems* (Dortrecht: Reidel) pp 13–32
 Boyer T H 1969 *Phys. Rev.* **182** 1374
 Brush S G 1966 *Kinetic Theory* vol 2 (Oxford: Pergamon) pp 88–175
 — 1976a *On the Kind of Motion We Call Heat* vols 1 and 2 (Amsterdam: North-Holland)
 — 1976b *On the Kind of Motion We Call Heat* (Amsterdam: North-Holland) ch 6, 12 and 14
 — 1976c *On the Kind of Motion We Call Heat* (Amsterdam: North-Holland) ch 15
 Chandrasekhar S 1943 *Rev. Mod. Phys.* **15** 1
 Einstein A and Besso M 1979 *Correspondence* (Paris: Hermann) p 291
 Feller W 1952 *Ann. Math.* **55** 468, 515
 ter Haar D 1954 *Elements of Statistical Mechanics* (London: Constable) appendix 1
 Klein M J 1973 *Acta Phys. Austriaca* Suppl. X 53–106
 Kramers H A 1940a *Physica* **7** 284 §2
 — 1940b *Physica* **7** 284 §2
 Kuhn T S 1978a *Black-body Theory and the Quantum Discontinuity 1894–1912* (Oxford: Clarendon) p 54
 — 1978b *Black-body Theory and Quantum Discontinuity 1894–1912* (Oxford: Clarendon) ch 2
 Marshall T W 1980 *Physica A* **103** 172
 — 1981 *Phys. Rev. D* **24** 1509
 — 1982 *J. Appl. Math. Phys. (ZAMP)*
 Smoluchowski M 1916a *Z. Phys.* **17** 557–71, 585–99 (Amsterdam: North-Holland)
 — 1916b *Z. Phys.* **17** 590 (footnote)
 Uhlenbeck G E 1927 *PhD Thesis, Leyden*
 Uhlenbeck G E and Ornstein L S 1930a *Phys. Rev.* **36** 823
 — 1930b *Phys. Rev.* **36** 839, note II
 Wang M C and Uhlenbeck G E 1945a *Rev. Mod. Phys.* **17** 338
 — 1945b *Rev. Mod. Phys.* **17** 341 note IV