

found good agreement with experiment from 4.2 K upward.

If there is a gap in the magnon spectrum at $k = 0$, as suggested by neutron scattering, the intensity of the optical absorption bands should begin to deviate from the T^2 law as the temperature becomes comparable to the gap energy. We therefore measured the sharp 632-nm band down to the limit of pumped ^4He , about 0.7 K.⁵⁸ Some of the results, obtained using a nitrogen laser pumped tunable dye laser⁵⁹ are shown in Figure 9. The sharp band at 631.3 nm, which dominates the band envelope at 3 K and upward, disappears rapidly below 1 K and can be quantitatively fitted to a gap energy equivalent to 1.0–1.5 K.

From these experiments we now have a good picture of the crystal and magnetic structures of the chlorochromates, the reasons why they are ferromagnetic, and the effect this has on their optical properties. Although

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they are the most visible transparent ferromagnets known at present, their relatively low Curie temperatures will limit technological application of their curious properties, whether to optical modulation or to magnetic data storage with optical readout. Nevertheless they have provided intriguing problems for magnetic theory and an object lesson in applying a wide range of physical techniques. A further dimension of chemical variation, only touched on in this account, concerns replacement of the alkali metal cations by organic groups, increasing the spacing between the layers up to as much as 25 Å.²⁰ With their simpler prototypes they too are good examples of how preparative inorganic chemistry can bring forward new systems to challenge the skills both of the experimental and of the theoretical physicist.

The experiments described here were carried out in collaboration with many colleagues, postdoctorates, and graduate students whose names appear in the references; my best thanks for all their help. Our group has been supported by the U.K. Science Research Council, A.E.R.E. Harwell, and the National Research Development Corporation.

Nonequilibrium Thermodynamics and the Stability of States Far from Equilibrium

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Received December 21, 1978

At equilibrium the three laws of thermodynamics—energy conservation, entropy maximization, and the inaccessibility of absolute zero—are the basis for understanding many relationships between experimental quantities.² Unfortunately, many of these relationships are valid only at equilibrium, since the Second Law is valid only for changes which end up at equilibrium.

In fact, a central problem in physical chemistry is this: Does there exist a generalization of the Second Law which is valid away from equilibrium? This is an old question having its origins in Boltzmann's work in gas kinetics,³ and many attempts have been made at answering it.⁴ In this Account, I will discuss a solution to this problem which is based on the dynamics of molecular fluctuations.⁵ These fluctuations are caused by the relentless motion involved in molecular processes and are intimately related to the stability of nonequilibrium systems.

The chief focus of this Account is nonequilibrium steady states⁶ of large collections of molecules. These

are states which have time-independent properties, even though mass, energy, or momentum is being transported through the system. Such states are in many ways like equilibrium states, yet they cannot be described by classical thermodynamics. Simple examples are the steady flow of fluid through a pipe or the steady dc current in an electrical resistor. More intricate, and fascinating, examples include systems which become unstable or begin to oscillate as the steady state is removed farther from equilibrium. Typical of these systems are the roll structure of Bénard cells in a layer of fluid heated from below,⁷ oscillating colors due to periodic changes in indicator concentrations in the Belousov reaction,⁸ or the periodic voltage and shape

(1) Permanent address: Department of Chemistry, University of California, Davis, CA 95616.

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(3) L. Boltzmann, "Lectures on Gas Theory", S. G. Brush, Translator, University of California Press, Berkeley, 1964.

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changes caused by changing surface tension in the "beating mercury heart".⁹

Although these instabilities have complicated kinetic descriptions, many of their features are illustrated by an instability which can occur in certain redox electrodes.¹⁰ In Figure 1 is a schematic diagram of an electrode which has a negative differential resistance. This may be caused by the electrodesorption of a critical intermediate in the redox process¹¹ or the coverage of the electrode by a passive film.¹² Using simple circuit theory, the rate of change of the voltage, V , across the electrode is given by¹³

$$CdV/dt = (E - V)/R - i(V) \quad (1)$$

where C is the electrode capacitance, R the external resistance, E the external voltage drop, and $i(V)$ the redox current. A steady state occurs when the voltage is independent of time. This means that $dV/dt = 0$, so eq 1 implies that

$$(E - V^{ss})/R = i(V^{ss}) \quad (2)$$

Equation 2 determines the voltage, V^{ss} , at steady state. This voltage can also be determined graphically in Figure 1 by looking for the intersections of the left- and right-hand sides of eq 2. Assuming that E is as shown in the figure, there can be three distinct situations. At low resistance $V^{ss} \approx E$ and there is only one steady state; at intermediate resistance there are three steady states; and, finally, at very high resistance again only one state. These are all nonequilibrium states unless the resistance is infinite, when the electrode receives no current from the external voltage source. In the equilibrium state no current flows, and the elementary processes of reduction and oxidation on the electrode are in balance.

As the resistance in the external circuit is increased, a "phase transition" like behavior appears in the voltage. This is because the voltages in the negative resistance region are *unstable*. This means that a voltage which is close to the steady-state value will not stay close to steady state but, like a pencil balanced on its point, move away.¹⁴ This can be seen mathematically by looking at how a deviation, from steady state, $v = V - V^{ss}$, which is small ($|v| \ll V^{ss}$), changes in time. Equation 1 and the Taylor series expansion

$$i(V) = i(v + V^{ss}) = i(V^{ss}) + (\partial i/\partial V)^{ss}v + \dots$$

give

$$Cd v/dt = (E - V^{ss})/R - v/R - i(V^{ss}) - (\partial i/\partial V)^{ss}v + \dots$$

But eq 2 shows that the first and third terms cancel, so a small deviation satisfies where

$$dv/dt = H v$$

$$H = -C^{-1}(1/R + (\partial i/\partial V)^{ss}) \quad (3)$$

Equation 3 gives the "linear stability analysis" of the steady state,¹⁴ and the relaxation rate of the voltage is given by the quantity H . This equation has the exponential solution

$$v(t) = \exp(Ht)v(0)$$

where $v(0)$ is the deviation at $t = 0$. This result is the key to linear stability analysis: because of the exponential, the initial deviation decreases to zero as time goes on when $H < 0$ but explodes to infinity when $H > 0$. Consequently the state is stable under the first condition but unstable under the second. Comparing Figure 1 and the definition of H shows that the steady states with a negative resistance are unstable. This is so since the slope of the straight line is $-1/R$, which is smaller in magnitude than the slope $(\partial i/\partial V)^{ss}$ of the dc current curve.

The instability gives rise to the abrupt transitions indicated by the arrows in Figure 2. This figure is constructed from Figure 1 by increasing the resistance, as shown by the decreasing slope of the three straight lines. Figure 2 shows the voltage at steady state as a function of the external resistance and the hysteresis which occurs because of the instability in the negative resistance region. The loop is like the van der Waal's loop which occurs in a liquid-gas-phase transition,^{15,16} but cannot be analyzed with thermodynamics since it does not occur at equilibrium.

Stability and Liapunov Functions

A general feature seen in the preceding example is that a steady state may become unstable as it is taken farther and farther from equilibrium. The linear stability analysis used in that example is only one of several ways to determine stability.¹⁴ Indeed, for systems with many variables the linear analysis becomes tedious since many exponentials are involved in the solution to the kinetic equations. In fact, one must solve a matrix eigenvalue problem that has the dimension of the number of variables.

A much simpler alternative for examining the stability of steady states was developed by Liapunov in the late 19th century.¹⁴ Liapunov looked at positive functions ϕ of the state variables which vanish at the steady state. Such a function acts like a distance function—measured with respect to the steady state. Liapunov proved that if near the steady state this function decreases as time goes on, then the steady state is stable. Functions ϕ that have this property are called "Liapunov functions". Liapunov also showed that if instead the function ϕ increased in time, the state was unstable.

For the electrochemical example in Figure 1 these results are illustrated by the function $\phi(v) = v^2/\sigma$, where σ is a positive constant. This function is positive and vanishes only when $v = V - V^{ss} = 0$. Using the chain rule to differentiate v^2 gives eq 4, where eq 3 is used in

$$d\phi/dt = (2v/\sigma)dv/dt = 2v^2H/C\sigma \quad (4)$$

the last equality. By definition, ϕ will be a Liapunov

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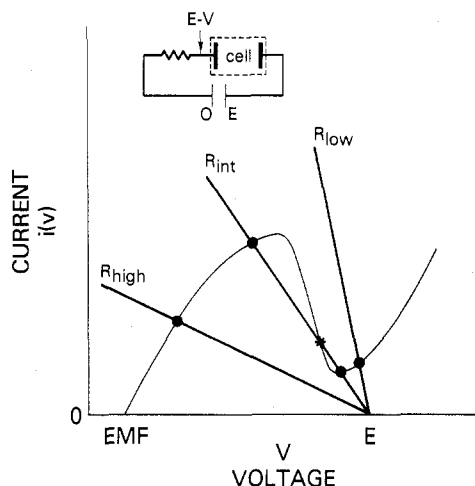


Figure 1. Schematic graph of current vs. voltage with circuit diagram inset for an electrode with a negative differential resistance. The straight lines represent $(E - V)/R$ for three values of R . The intersections are the steady states with the circles stable and the star unstable.

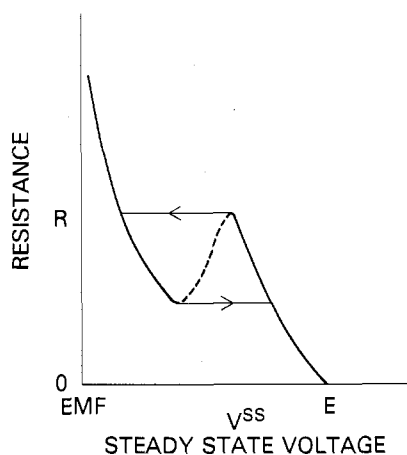


Figure 2. First-order phase-transition-like behavior for the electrode in Figure 1. The van der Waals type loop shows hysteresis at the minimum and maximum as the resistance is decreased and then increased.

function for the steady state if $d\phi/dt < 0$. Since $v^2/C\sigma$ is never negative, this will be the case whenever $H < 0$. Liapunov's theorem then implies that the steady state is stable whenever $H < 0$. Similarly, eq 4 implies the inequality $d\phi/dt > 0$ for steady states with $H > 0$. Again by Liapunov's theorem such states are unstable. These are precisely the conditions for stability obtained by the linear stability analysis of this problem, which verifies Liapunov's theorem for this example.

It is worth adding a caveat about the use of Liapunov's theorem. Just because a given positive function has a time derivative of mixed sign (positive for some deviations and negative for others), this in no way "threatens" stability. Indeed, for a given positive ϕ , the Liapunov criterion $d\phi/dt < 0$ is *sufficient* to imply stability, but not *necessary*. Consequently its violation in the form $d\phi/dt > 0$ implies nothing.

Failure of the Local Equilibrium Theory Far from Equilibrium

A valid extension of classical thermodynamics which works very close to equilibrium involves local equilibrium thermodynamic functions. For example, in an ideal gas undergoing the chemical reaction $H_2 + D_2 =$

$2HD$, the chemical potential of hydrogen is¹⁷

$$\mu_{H_2} = \mu_{H_2}^\circ + k_B T \ln \rho_{H_2} \quad (5)$$

with k_B Boltzmann's constant, T the absolute temperature, ρ_{H_2} the number density of H_2 , and $\mu_{H_2}^\circ$ the standard-state chemical potential. Even though such a gas, evidently, has three independent molecular species (H_2 , D_2 , and HD), equilibrium thermodynamics involves only two independently variable densities.² This is because the condition of equilibrium determines one of the densities once the other two are known. Nevertheless, the Second Law involves the local equilibrium thermodynamic functions, and changes in the Helmholtz free energy at constant temperature and volume are written

$$dA = \mu_{H_2} dN_{H_2} + \mu_{D_2} dN_{D_2} + \mu_{HD} dN_{HD} \quad (6)$$

In eq 6 the N 's are the number of the subscripted molecules and the chemical potentials are the local equilibrium ones as in eq 5. Equation 6 involves an extension of thermodynamics to a state just slightly out of equilibrium and is used, for example, in showing¹⁷ that the thermodynamic form of the equilibrium constant is

$$\rho_{HD}^{e2} / \rho_{H_2}^e \rho_{D_2}^e = \exp([\mu_{H_2}^\circ + \mu_{D_2}^\circ - 2\mu_{HD}^\circ] / k_B T)$$

The success of the local equilibrium theory close to equilibrium might suggest that it can also be used in the neighborhood of far from equilibrium steady states.¹⁸ A little reflection shows this hope to be vain since there is no Second Law or maximum principle for the usual thermodynamic functions near steady state. In fact, what is needed at steady state is a Liapunov function since that is exactly what the Second Law provides at equilibrium.

That the entropy is a stability function actually preceded Liapunov's work and is found already in Boltzmann's H theorem.³ However, its occurrence in local equilibrium thermodynamics was pointed out by Glansdorff and Prigogine.¹⁸ Their ideas concerned the second differential of the local equilibrium entropy, $\delta^2 S$. This is nothing more than the quadratic term in a Taylor series expansion of the entropy around equilibrium, viz.

$$\begin{aligned} S(n_1, n_2, \dots, n_k) &= S(n_1^e, n_2^e, \dots, n_k^e) + \sum_i (\delta S / \delta n_i)^e a_i + \\ &\quad \frac{1}{2} \sum_{ij} (\delta^2 S / \delta n_i \delta n_j)^e a_i a_j + \dots \quad (7) \\ &\equiv S^e + \delta S + (1/2) \delta^2 S + \dots \end{aligned}$$

where n_i is an extensive variable, n_i^e is its equilibrium value, and $a_i = n_i - n_i^e$. Because the entropy is maximized at equilibrium, δS is identically zero and

$$\delta^2 S \leq 0 \quad (8)$$

(that is, $S \leq S^e$ for a maximum). The Second Law of thermodynamics, namely the increase of the entropy $dS/dt \geq 0$, can thus be written close to equilibrium using eq 7 as

$$d\delta^2 S / dt \geq 0 \quad (9)$$

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This means that the quadratic form $-\delta^2S$ is positive and vanishes at equilibrium (where $a_j \equiv 0$) and that $-d\delta^2S/dt \leq 0$. Hence the second differential of the local equilibrium entropy is a Liapunov function¹⁸—at least very close to equilibrium.

The attempts¹⁸ to use the local equilibrium entropy as a central principle far from equilibrium failed.¹⁹ Mathematically this failure is due to the fact that Liapunov's theorem provides only a sufficient condition for stability.^{14,19} Consequently even though δ^2S may not be a Liapunov function, this in no way affects the stability of a state. This situation often occurs because the sign of $d\delta^2S/dt$ can be either positive or negative far from equilibrium.²⁰ The attempt to use a local equilibrium theory far from equilibrium also fails on physical grounds. This is because it relies on the form of a thermodynamic function, the entropy, which has no Second Law associated with it far from equilibrium.

Molecular Fluctuations

A different attack on the problem of thermodynamic functions away from equilibrium is based on molecular fluctuations. These fluctuations are the incessant small variations of physical quantities in time and space caused by molecular motion. Fluctuations occur even in systems that are at thermodynamic equilibrium and were first noticed by Brown²¹ in 1827. Using a light microscope Brown observed that pollen grains in a drop of water move about in a strange, chaotic manner. The cause of this motion was not explained conclusively until Einstein's famous work 80 years later. Einstein attributed the jagged paths to random fluctuations in the number and direction of collisions between the water molecules and the molecules of the Brownian particle. His quantitative predictions were soon verified by Perrin and lead, among other things, to an independent measurement of Avogadro's number.

Because collisions underlie all phenomena involving collections of molecules, it should be clear that all physical quantities fluctuate in a large system. For example, the reaction $\text{Be}^{2+} + \text{SO}_4^{2-} = \text{BeSO}_4$ in aqueous solution involves molecular encounters mediated by H_2O . Although chemists are accustomed to thinking that the concentrations of these species do not change at equilibrium, this is true only on the average. At any instant of time, the details of the ongoing molecular encounters will dictate how beryllium is distributed between its ionic and molecular forms. Thus the chemical reaction leads to fluctuations in the concentrations of Be^{2+} , SO_4^{2-} , and BeSO_4 . Although small, these fluctuations are observable and have been measured by means of the fluctuating current which they produce in an electrolytic cell.²² Similarly the instantaneous amount of solute in a fixed region of solution is a random function of time at equilibrium. These sorts of concentration fluctuations are caused by the molecular process of diffusion. They have been measured quantitatively by using the fluctuating

fluorescence induced by a light beam passed through solution.²³

Just as Einstein was able to develop a theory of Brownian motion, Onsager,²⁴ Landau,²⁵ and others²⁶ have developed a quantitative theory of fluctuations for thermodynamic variables at equilibrium. In fluids, fluctuations in the local internal energy, concentrations, and momentum can be observed by light-scattering experiments.²⁷ These experiments can be performed using light of a given frequency with the angular distribution of the scattered light being measured. This leads to information about the static fluctuations, which describe the variety of thermodynamic environments seen by the light ray as it traverses the fluid. The dynamic fluctuations, on the other hand, describe how a fluctuation relaxes back toward equilibrium and can be measured using frequency-dependent light scattering.

The theories of thermodynamic fluctuations at equilibrium compare well with the results of light scattering²⁷ and other measurements.^{28,29} There is, however, a serious problem in extending the theory away from equilibrium. The stumbling block is the fact that the theory relies heavily on the Second Law of thermodynamics,²⁶ which does not hold for a driven system away from equilibrium.

Properly generalizing the theory of fluctuations requires adopting a more explicitly molecular point of view.^{5,30} This is necessary since, as we have seen, fluctuations are caused by the motion of molecules. Molecular motion is also responsible for dissipative processes such as diffusion, heat transport, and chemical reaction. Consequently, it should not be surprising that a close relationship exists between dissipation and fluctuations.³⁰

To see more clearly what this is, consider an elementary molecular process. An example familiar to chemists is an elementary chemical reaction³¹ which involves direct reactive collisions between molecules. Because it is an elementary process, it will involve both direct (forward) and restoring (reverse) molecular events. Such a molecular process has a forward rate V^+ , has a reverse rate V^- , and will change the extensive variable n_j by an amount ω_j . In chemical reactions, for example, the ω_j 's are the stoichiometric coefficients, taken positive for products and negative for reactants, and n_j is the number of molecules of a given kind. The rates of an elementary process cause a perpetual increase in the entropy of a system, except at equilibrium where the forward and reverse rates are equal. This is reflected in the fact that the nonlinear generalization of Rayleigh's dissipation function is always positive, except at equilibrium where it vanishes.³²

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The crucial point here is that these same elementary molecular processes determine the fluctuations in a system.³⁰ For example, in Langevin's conception of Brownian motion³³ collisions cause a particle to move by creating a random force on it. This can be reinterpreted using Newton's law, which states that a force is equivalent to the time rate of change of momentum. Thus the random force can be thought of as a random component of the time derivative of the momentum. Similarly the randomness in any elementary process will produce a random component, \tilde{f}_i , to the time derivative of the extensive variable, n_i . For the elementary reaction $\text{Be}^{2+} + \text{SO}_4^{2-} \rightleftharpoons \text{BeSO}_4$ this will produce a random term in the rate equation for Be^{2+} and SO_4^{2-} ions. In the fluctuation-dissipation theory,⁵ the product of these random "forces", $\tilde{f}_i \tilde{f}_j$, averaged over a short time interval is given by eq 10^{5,30,34} where κ labels different

$$\gamma_{ij} = \sum_{\kappa} \omega_{\kappa} (V_{\kappa}^{+} + V_{\kappa}^{-}) \omega_{\kappa j} \quad (10)$$

elementary processes and i and j refer to different extensive variables. Equation 10 relates the fluctuations to the rates of the dissipative process and is a basic principle of the fluctuation-dissipation theory. In the older theories of equilibrium fluctuations,²⁷⁻²⁹ the strength of the fluctuation term γ was deduced from a knowledge of the local equilibrium entropy.

The connection between dissipation and fluctuations given in eq 10 and the principle that fluctuations around the conditional average are a nonstationary, Gaussian process form the basis of the fluctuation-dissipation theory of molecular fluctuations.^{5,30,35} When applied at steady state,⁶ the theory shows that the probability distribution of extensive variables around a stable steady state is a Gaussian, or normal, distribution. The Gaussian is centered at the steady state predicted by the usual kinetic analysis, as described, for example, by eq 1 and 2. The width of the Gaussian is determined by the fluctuation-dissipation theorem⁶

$$H\sigma + \sigma H^T = -\gamma \quad (11)$$

Equation 11 is a matrix equation with

$$\sigma_{ij} = \langle (n_i - n_i^{ss})(n_j - n_j^{ss}) \rangle^{ss}$$

the average square of the deviations from steady state. For instance, if n_i is the number of molecules in a small region of space located at position \mathbf{r}_i , then σ_{ij} is proportional to the density-density correlation function. It is this function that determines the static light scattering spectrum.³⁴ The remaining quantities in eq 11 are the matrix γ , which is defined by eq 10; H , the linearized matrix of the average kinetic equations (cf. the electrochemical example in eq 3); and H^T , the transpose of H . Indeed, H is precisely the matrix whose eigenvalues determine the linear stability analysis.

This kinetic theory of fluctuations reduces to the thermodynamic theory of fluctuations near equilibrium,²⁴⁻²⁶ a theory which is supported by numerous experimental investigations.²⁷ The fluctuation-dissipation theory has been used to give an accurate calculation³⁶ of the measured³⁷ voltage fluctuations in

the far-from-equilibrium Gunn instability and is further supported by work on the thermodynamic limit of the master equation theory of fluctuations.³⁸

Liapunov Stability and Fluctuations

The local equilibrium entropy theory of stability^{18,20} fails because it is not associated with a second law type maximum principle away from equilibrium. Indeed, if the spirit of Boltzmann's work is correct, one should seek the Liapunov stability principle first and then let the thermodynamic functions rest on this basis.

The key to obtaining a Liapunov function at steady states⁶ comes from the fluctuation-dissipation theorem in eq 11. According to linear stability analysis¹⁴ a deviation around steady state of the extensive variables will, as in eq 2, evolve in time according to

$$da_i/dt = \sum_j H_{ij} a_j \quad (12)$$

where $a_j = n_j - n_j^{ss}$ the deviation from the steady state. When the eigenvalues of H have negative real parts, the steady state is stable. On the other hand, eq 11 is known⁶ to generate a Liapunov function for eq 12. In fact, when γ is a positive definite matrix, a *necessary and sufficient* condition for the steady state to be stable is³⁹ that eq 11 have a positive definite solution matrix σ . Actually, it is easy to understand this result in words: the matrix σ is related to the spread of the Gaussian distribution of fluctuations at steady state. Fluctuations are caused by molecular motions which are constantly exploring the neighborhood of the steady state. If a steady state is stable, the fluctuations will spread out within a fixed domain and σ will be finite. On the other hand, if the state is unstable, the fluctuations will not settle down near the steady state, the width of the probability distribution will tend to infinity,⁶ and eq 11 will have no solution.

This relationship between stability and fluctuations can be seen in an elementary manner when fluctuations in only a single variable are significant. As an example, consider voltage fluctuations for the redox electrode discussed in the introduction. For this model all the quantities in eq 11 are scalars (e.g., $H = H^T$, a number), and the equation is easily solved:

$$\sigma = \langle (\delta v)^2 \rangle = -\gamma/2H$$

This shows that the width of the voltage fluctuations, as measured by $\sigma^{1/2}$, is inversely proportional to $H^{1/2}$. But according to the linear stability analysis (cf. eq 3), H is negative for stable steady states and positive for unstable steady states. Consequently, for a stable state the width, $\sigma^{1/2}$, exists and is positive. However, as the external resistance is tuned toward the unstable points (i.e., the maximum or minimum in Figure 2), H approaches zero. The preceding formula then shows that the width of the voltage fluctuations approaches infinity and that eq 11 has no solution.

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The voltage fluctuations near the Gunn instability have been examined³⁶ by means of an analysis related to this. The Gunn instability occurs when an external current of the order of 1 A is applied across a thin crystal of GaAs. The current produces an electric field of about 4×10^3 V/cm and leads to microwave oscillation when the field exceeds a critical value. Measurements of the voltage fluctuations³⁷ across GaAs have verified that their distribution is Gaussian and that the width of the Gaussian increases rapidly as the point of instability is reached. This agrees qualitatively with the results described above. The detailed calculations applied to the elementary process of electron diffusion give results which are in quantitative agreement with experiment.³⁶

The σ Function

A consequence of the mathematical results described in the preceding section is that the quadratic form

$$\phi = \sum_{ij} a_i \sigma_{ij}^{-1} a_j \quad (13)$$

is a Liapunov function for the steady state,⁶ where the superscript -1 means the inverse matrix. This result is a generalization to many variables of the Liapunov function v^2/σ for the redox electrode instability in the introduction. The important point, however, is that this particular quadratic form is related to the static fluctuations around steady state. Indeed, their distribution has the Gaussian⁶ form

$$W(\mathbf{a}) \sim \exp(- (1/2) \sum_{ij} a_i \sigma_{ij}^{-1} a_j) \quad (14)$$

These fundamental formulas are completely analogous to the results which hold at equilibrium. At equilibrium eq 13 reduces to the fact that the second differential of the entropy, $\delta^2 S$, is a Liapunov function and eq 14 becomes the Einstein formula

$$W^e(\mathbf{a}) \sim \exp(\delta^2 S / 2k_B)$$

where the superscript e means equilibrium.

To complete this analogy, it was necessary to find a function of state which had a second differential proportional to the expression in (13).^{6,40} Such a function, called the σ function or Σ , does exist and can be defined by the differential equation

$$\delta^2 \Sigma / \delta n_i \delta n_j = -k_B \sigma_{ij}^{-1} \quad (15)$$

Notice that this relationship involves second, rather than first, derivatives as are used to define the entropy at equilibrium. A relationship analogous to eq 15 holds for the entropy at equilibrium, and in order to combine equilibrium and nonequilibrium states within a single definition, the use of second differentials appears to be necessary. Moreover, when defined in this way, eq 13 and 14 imply that $\delta^2 \Sigma$ is a Liapunov function and that the probability distribution is given by

$$W(\mathbf{a}) \sim \exp(\delta^2 \Sigma / 2k_B)$$

To ensure that the definition in eq 15 is proper, it must be shown that this differential equation is consistent. This requires that it can be solved and that the σ function reduce to the local equilibrium entropy at full equilibrium. In taking care of these technicalities it is necessary to give consideration to a new collection

of variables on which steady-state thermodynamic functions will depend.³⁸ For example, the steady states of the redox electrode considered in the introduction require a knowledge of the current imposed by the external circuit. More generally, there will exist inputs or fluxes, \mathbf{f} , of mass, energy, and momentum which characterize the steady state, as well as other external parameters, \mathbf{R} , such as the temperature of reservoirs, which are relevant to maintaining the steady state. The resulting integration of eq 15 produces the σ function whose functional dependence can be written⁴⁰

$$\Sigma(\mathbf{n}; \mathbf{f}, \mathbf{R}) = S(\mathbf{n}) + \sum_j f_j v_j(\mathbf{n}; \mathbf{f}, \mathbf{R}) \quad (16)$$

Since at equilibrium all the fluxes, f_j , vanish, eq 16 shows that at equilibrium Σ becomes the local equilibrium entropy. The functions v_j , which are new intensive variables, arise because of nonequilibrium contributions to the fluctuations at steady state. The σ function is a generalization of the local equilibrium entropy and has properties near steady state which are analogous to the properties of the entropy near equilibrium.

For a number of systems whose kinetic equations are linear, the σ function has no nonequilibrium contribution.⁶ These include certain models of membrane transport and the generalized free-energy transduction mechanisms considered by Hill.⁴¹ However, for linear systems with additive inputs or those with nonlinear kinetics—which, therefore, have interesting nonequilibrium behavior—the nonequilibrium contributions are vital.^{6,40,42} These results clearly demonstrate that the simple extension of the Einstein formula to nonequilibrium steady states lacks generality.^{18,20}

The variables which are “conjugate”⁴² to the extensive thermodynamic variables at steady state can be obtained from Σ . They are defined by^{6,38}

$$\phi_i = \delta \Sigma / \delta n_i = \delta S / \delta n_i + \sum_j f_j \delta v_j / \delta n_i \quad (17)$$

These quantities are intensive variables and provide a nonequilibrium thermodynamic generalization of chemical potentials, temperatures, and other of the usual intensive thermodynamic quantities. It should be noted that the σ function is an extensive variable,⁴⁰ just like the entropy. In fact, the extensive variables are the so-called “natural variables” for the entropy because its dependence upon them produces a complete set of thermodynamic information. Similarly the natural variables for Σ are the usual extensive variables, \mathbf{n} , the extensive fluxes, \mathbf{f} , and (possibly) intensive reservoir variables, \mathbf{R} . Because Σ is an extensive variable, it is possible to derive a Gibbs–Duhem-like relationship between the intensive variables ϕ_i , $\delta \Sigma / \delta f_i$, and R_i . Finally, it is possible to reexpress the σ function in terms of some of these intensive variables, just as one might use the entropy as a function of temperature and pressure at equilibrium. This is purely a matter of convenience.

The Maximum Principle at Steady State

In equilibrium thermodynamics the Second Law implies that the entropy is maximized at equilibrium

(41) T. L. Hill, “Free Energy Transduction in Biology”, Academic Press, New York, 1977.

(42) J. Keizer, *J. Chem. Phys.*, **67**, 1473 (1977).

(43) H. B. Callen, “Thermodynamics”, Wiley, New York, 1962.

for an isolated system.² Similarly if a system is in contact only with a heat bath, the Helmholtz free energy of the system is minimized if the temperature of the system is maintained at the temperature of the bath. Other extremum principles are valid for other types of external environments at equilibrium. Indeed all of these results can be summarized using Massieu functions for the system of interest. These functions are Legendre transformations of the entropy⁴⁰ of the system and the general result is that the Massieu functions achieve their maximum at equilibrium under the appropriate interactions with reservoirs.

It should be clear that the σ function, being a generalization of the entropy, is not maximized at steady state since steady states involve contact with the outside. However, it can be shown that the appropriate Legendre transforms of the σ function are maximized at steady state. Here the importance of external fluxes and reservoirs becomes apparent since changes in which these quantities are fixed must be considered.

Using eq 16 and 17, the time derivative of Σ can be calculated to be⁴⁰

$$d\Sigma/dt = \sum_j \phi_j dn_j/dt$$

when \mathbf{f} and \mathbf{R} are fixed. It can be shown that the sign of this expression can be positive or negative, so the σ function is not maximized at steady state. Indeed, what is needed for a system in contact with the environment is a generalization of the Clausius inequality²

$$dS/dt - (dQ/dt)(1/T)_R \geq 0$$

where dQ/dt is the heat flux. This inequality, it will be recalled,² is valid for a reversible or irreversible process involving a reservoir at temperature T_R . A generalization of the Clausius inequality can be gotten from the second differential of the σ function. A direct consequence of its definition is that⁴⁰

$$(1/2)d\delta^2\Sigma/dt = \sum_j \phi_j dn_j/dt - \sum_j \phi_j^{ss} dn_j/dt \geq 0 \quad (18)$$

Finally, using eq 16, this can be written

$$d\Sigma/dt - \sum_j \phi_j^{ss} dn_j/dt \geq 0 \quad (19)$$

Equation 19 is the generalization of the Clausius inequality and permits the proof that Legendre transformations of Σ are maximized at steady state.

To see this, consider a process which fixes the intensive variables ϕ_j at their steady state value as well as fixing the fluxes, \mathbf{f} , and reservoir variables, \mathbf{R} . Under

these conditions eq 19 becomes⁴⁰

$$d(\Sigma - \sum_j \phi_j n_j)/dt \geq 0$$

i.e., the Legendre transformation of the σ function, $\Sigma - \sum_j \phi_j n_j$, is an increasing function of time, achieving its maximum at steady state.

The maximum principle requires that the intensive variables ϕ_j are maintained at their steady-state values. But ϕ_j is a function of the extensive variables, the fluxes, and reservoir variables—the latter two of which are fixed. Thus the ϕ_j can remain unchanged only when certain changes in the extensive variables cause no change in all the ϕ_j . This is similar to what happens at equilibrium where chemical reactions proceed at fixed temperature and have the effect of minimizing the Helmholtz free energy.² Similarly, at steady state, processes like internal relaxation of solvent molecules can occur at fixed values of the intensive variables, fluxes, and reservoir variables and would lead to an increase in the Legendre transformation of Σ .⁴⁰

Conclusion

The theoretical developments outlined in this Account present an attempt at generalizing classical thermodynamics so that it is applicable at nonequilibrium steady states. The approach is based on molecular fluctuations and leads to a theory which is in close correspondence to the classical theory. The basic idea is that fluctuations determine the stability of a system through the fluctuation-dissipation theorem and that the resulting Liapunov function has a thermodynamic significance. The development shows how new nonequilibrium variables, such as fluxes, need to be incorporated at steady state and gives rise to a systematic description of maximum principles.

At steady states the σ function, which generalizes the entropy, depends on nonclassical thermodynamic quantities, such as rate constants. This means that at steady states more detailed molecular information is available in the thermodynamics than at equilibrium. The theory is firmly based in macroscopic measurements since all the quantities of the theory can be determined by the measurement of fluctuations at steady state. As these measurements become more common and more sophisticated, the theory outlined here should come to be useful.

The work described in this Account was supported in part by grants from the National Science Foundation and a sabbatical leave from the University of California, Davis.