Nonequilibrium Statistical Thermodynamics

by

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Abstract

Keizer's approach to nonequilibrium statistical thermodynamics is reviewed. A canonical formulation of nonequilibrium processes was developed. Using the covariances of the fluctuations instead of the excess entropy production, a Lyapunov function for steady states was constructed. With it, Keizer created a thermodynamics for stable steady states that generalized the thermodynamics of equilibria. Subsequent studies of the interplay of chaos and fluctuations led to the observation that chaos amplifies fluctuations. The growth rate of the variances is initially exponential for a chaotic system and the exponential rate is twice the local Lyapunov exponent. This fact leads naturally to a formulation of quantum chaos that yields the classical Lyapunov exponent as a quantum signature of classical chaos.

I. Introduction

For a period of nearly twenty years (roughly 1970-1990), Joel Keizer's principal research interest was nonequilibrium statistical thermodynamics. This subject was not a goal in itself but served as the foundation for his real interest, the thermodynamics of metabolism in organisms. In the last decade of his life, the 1990's, his focus was almost exclusively on mathematical biology. Although his work was not on metabolism *per se*, the earlier work played a major role in his outlook and methodology.

The nonequilibrium thermodynamics stage of Keizer's research culminated in his very successful monograph: *Statistical Thermodynamics of Nonequilibrium Processes* (Keizer, 1987a). As a measure of its critical success, the book was translated into Russian by Yu. L. Klimontovich in 1990 (Klimontovich, 1990). The book was the synthesis of many years of study of nonequilibrium systems of many kinds. Chemical reactions and the importance of diffusion in diffusion controlled reactions were two topics to which Keizer devoted much attention during this period (Keizer, 1982; Keizer, 1987b). His reputation as a theoretical chemist grew rapidly with this work. That these two papers have had a major impact has been made evident by the great many citations they have received.

Fluctuations play the dominant role throughout Keizer's thermodynamic work. This is because their moments and correlations contain incredible amounts of information about the system in which they occur. This information can be gleaned from light scattering measurements in many instances (Berne & Pecora, 1976). Near full equilibrium, system fluctuations are governed by the entropy according to the Boltzmann-Planck formula (Planck, 1923). Since the entropy is a maximum at equilibrium and obeys the second law of thermodynamics, the second differential of the entropy near equilibrium serves as a Lyapunov function for the stability of equilibria (Callen, 1985). This fact is closely connected to the LeChatelier-Braun principle (Callen, 1985; Keizer, 1987a). An attempt was made by Glansdorff and Prigogine to extend the stability properties associated with the entropy to far from equilibrium states (Glansdorff & Prigogine, 1971). Although, flawed in its original form (Keizer & Fox, 1974; Fox, 1980), this attempt inspired Keizer to find a proper Lyapunov function for the stability of far from equilibrium steady states. This he ultimately succeeded in doing and he was able to formulate a complete thermodynamics of stable steady states as a result.

Keizer's monograph (Keizer, 1987a) ends with a chapter on chaos. Working together with the author, it was observed that there is a deep connection between chaos and fluctuations (Fox & Keizer, 1990; Fox & Keizer, 1991; Keizer et al., 1993). Fluctuations initially grow exponentially when the system is operating chaotically. The initial rate of exponential growth is twice the largest local Lyapunov exponent (Fox & Keizer, 1991).

By making measurements of the growth rate of the covariances of the fluctuations, the local Lyapunov exponent can be determined. Keizer spent the rest of his scientific career with work in mathematical biology. Fox extended the amplification of fluctuations by chaos ideas into the quantum chaology regime (Fox, 1990; Fox & Elston, 1994a; Fox & Elston, 1994b). He showed that the classical Lyapunov exponent is a quantum signature of classical chaos and that it can be measured by observing the growth rate of quantum covariances.

In section II of this paper, the canonical formulation of Keizer's theory of nonequilibrium thermodynamics is presented. In section III, the thermodynamics of steady states is developed. In section IV, the amplification of fluctuations by chaos is reviewed.

II. Keizer's Canonical Form

Three levels of description are found in physical theories: the microscopic, the macroscopic and the mesoscopic. The classical mechanics of particle dynamics and quantum mechanics are examples of microscopic physics. Hydrodynamics and thermodynamics are examples of macroscopic physics. In between is the less commonly used level of description, the mesoscopic, perhaps historically best exemplified by the Boltzmann equation. One can't really derive the Boltzmann equation from the microscopic Newtonian laws for myriads of particles, but one can make it quite plausible, and one can derive hydrodynamics from it. This shows that there can be hierarchies of levels of description from the microscopic to the macroscopic (Keizer, 1987a). Through studies of the fluctuating Boltzmann equation (Fox & Uhlenbeck, 1970) and of master equation treatments of chemical reactions (van Kampen, 1961; Keizer, 1977; Keizer & Conlan, 1983), Keizer developed a phenomenological mesoscopic theory for spontaneous fluctuations in macroscopic systems (Keizer, 1975; Keizer, 1976a). This was a very difficult task. It required abstracting the common features of a variety of different specialized treatments of physical and chemical phenomena, expressing them in a "canonical form" and then demonstrating by comparison with experiment that the resulting theory is correct. Few scientists have either the courage or the intellect for such a daunting task.

Keizer's theory begins with the idea of "elementary processes" (Keizer, 1987a). Label the different types of microscopically elementary processes in a system by the index κ. Every elementary process involves basic forward and reverse steps during which molecular-size amounts of some extensive variable, n_i, are changed in the forward or reverse directions. Using superscripts + or - for forward or reverse respectively, this situation is symbolized by

$$\left(n_{\kappa 1}^{+}, n_{\kappa 2}^{+}, \ldots\right) \underset{\leftarrow}{\overset{\rightarrow}{}} \left(n_{\kappa 1}^{-}, n_{\kappa 2}^{-}, \ldots\right) \tag{1}$$

The extensive variable n_i changes during the elementary process κ by the amount

$$\omega_{\kappa i} = n_{\kappa i}^{-} - n_{\kappa i}^{+} \tag{2}$$

The transition rate for an elementary process is given by the canonical form

$$V_{\kappa}^{\pm} = \Omega_{\kappa}^{\pm} \exp\left[-\sum_{j} \frac{F_j n_{\kappa j}^{\pm}}{k_B}\right] \tag{3}$$

in which k_B is Boltzmann's constant, $\Omega_{\kappa}^{\pm}$ are the intrinsic rates of the forward and reverse steps of the elementary process κ and the F_j's are intensive variables defined in terms of the local entropy, S(**n**), by

$$F_j = \frac{\partial S}{\partial n_j}$$

(4)

As Keizer pointed out (Keizer, 1987a), "canonical" means "established by canon" and describes a general rule with wide applicability, i.e. refers to a "phenomenological inference" and is not derived from any underlying microscopic dynamical theory. Thus, the canonical form theory was presented as a set of three postulates. These are: Postulate I. the deterministic equation is

$$\frac{d\overline{n}_i}{dt} = \sum_{\kappa} \omega_{\kappa i}\left(\overline{V}_{\kappa}^{+} - \overline{V}_{\kappa}^{-}\right) + \overline{S}_i \equiv \overline{R}_i$$

(5)

in which the over-bar denotes the conditional average of the quantity and S_i is the i^{th} component of the streaming term; Postulate II. the linearized equation for the fluctuations is

$$\frac{d\delta n_i}{dt} = H_{ij}(\overline{\mathbf{n}},t)\delta n_j + \tilde{f}_i(t)$$

(6)

in which

$$H_{ij}(\overline{\mathbf{n}},t) = \frac{\partial \overline{R}_i}{\partial \overline{n}_j}$$

(7)

$\delta n_i = n_i - \bar{n}_i$ and $\tilde{f}_i(t)$ is a fluctuation of gaussian Markov type satisfying correlation formulae

$$< \tilde{f}_i(t) > = 0$$

$$< \tilde{f}_i(t)\tilde{f}_j(t') > = \gamma_{ij}(\bar{\mathbf{n}})\delta(t - t') \tag{8}$$

where $\delta(t - t')$ is the Dirac delta function; and Postulate III. the fluctuation-dissipation relation

$$\gamma_{ij}(\bar{\mathbf{n}}) = \sum_{\kappa} \omega_{\kappa i}\left(\bar{V}_{\kappa}^{+} + \bar{V}_{\kappa}^{-}\right)\omega_{\kappa j} \tag{9}$$

This theory reduces to the Onsager theory (Onsager, 1931a; Onsager, 1931b) close to full equilibrium. In addition, Keizer has applied it to: the Boltzmann equation, chemical reactions, diffusion, hydrodynamics, ion transport, electric circuits, electrode processes, lasers and other systems. That each of these disparate systems can be subsumed by a single theoretical description is a remarkable achievement.

III. Generalized Thermodynamics of Stable Steady States

The entropy near full equilibrium gives rise to a Lyapunov function for the stability of the equilibrium states. Since the entropy is a maximum at equilibrium and the second law of thermodynamics implies that the entropy is monotonically increasing with time, it follows that the second differential of the entropy, $\delta^2 S$, satisfies

$$\delta^2 S \leq 0 \quad and \quad \frac{d}{dt}\delta^2 S \geq 0 \tag{10}$$

This is a sufficient condition for the stability of equilibrium. In an attempt to extend this result to far from equilibrium steady states, Glansdorff and Prigogine (Glansdorff & Prigogine, 1971) used the local equilibrium entropy. Even though $\delta^2 S \leq 0$ still holds true, $\frac{d}{dt}\delta^2 S \geq 0$ no longer is true because the second law is no longer valid far from equilibrium (Keizer, 1979). Indeed, the sign of this derivative is indefinite far from equilibrium and because the Lyapunov function is only sufficient and not necessary for stability, this indefiniteness in no way "threatens" stability (Keizer, 1979; Lavenda, 1985). This subtlety is the basic point of the paper of Keizer and Fox (Keizer & Fox, 1974) and was ignored by Glansdorff et al. (Glansdorff et al., 1974) but was later recognized by Prigogine (Prigogine, 1978).

In spite of the heat generated by this debate at the time, Keizer was motivated by the attempt of Prigogine et al. to find a valid candidate for a Lyapunov function for stable steady states. The key insight leading to his success in this goal was recognizing the underlying importance of the fluctuations. Near full equilibrium, the entropy governs the fluctuations but far from equilibrium this connection breaks down. It is the properties of the fluctuations that give rise to a Lyapunov function. Keizer (Keizer, 1979) followed the spirit of Boltzmann's work and concluded that the thermodynamic functions should depend upon the Lyapunov function and not the other way around. Let the deviation of variable n_i from its steady state value, n_i^{ss} be denoted by $a_i = n_i - n_i^{ss}$. From equations paralleling Eqs. (6) and (8), it follows that the steady state correlation matrix defined by

$$\sigma_{ij}^{SS} = < a_i a_j > \tag{11}$$

satisfies

$$H_{ik}\sigma_{kj}^{SS} + \sigma_{ik}^{SS} H_{kj}^{T} = -\gamma_{ij} \tag{12}$$

where the superscript T denotes the adjoint and repeated indices are summed. The steady state probability distribution has the form

$$W(\mathbf{a}) \approx \exp\left[-\frac{1}{2}\sum_{i,j} a_i (\sigma^{SS-1})_{ij} a_j\right]$$

$$(13)$$

At full equilibrium, this expression reduces to the Einstein formula

$$W^e(\mathbf{a}) \approx \exp\left[\frac{\delta^2 S}{2k_B}\right] \tag{14}$$

Thus, to complete the analogy with full equilibrium, it was necessary to find a function of state, Σ, that had a second differential proportional to the argument of the exponential in Eq. (13), i.e. such that

$$\frac{\partial^2 \Sigma}{\partial n_i \partial n_j} = -k_B \sigma_{ij}^{SS-1} \tag{15}$$

Keizer called this function the "sigma-function" and showed that Eq. (15) could be integrated (Keizer, 1979; Keizer, 1987a) giving the general form

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

in which S is the local entropy, f_i is a component of the extensive inputs and R_i is a component of the intensive reservoir parameters. Both types of variables are relevant in maintaining a far from equilibrium steady state. The intensive variables, ϕ_i, conjugate to the extensive thermodynamic variables, n_i, are given by

$$\phi_i = \frac{\partial \Sigma}{\partial n_i} = \frac{\partial S}{\partial n_i} + \sum_j f_j \frac{\partial v_j}{\partial n_i}$$

(17)

These quantities provide a nonequilibrium thermodynamic generalization of temperature, chemical potential and other intensive thermodynamic quantities (Keizer, 1976b; Keizer, 1978; Keizer, 1984; Keizer, 1985). The new terms are corrections to local equilibrium quantities caused by the system having been driven to a far from equilibrium steady state (Keizer, 1987a).

Not satisfied with mere formalism, Keizer decided to do an experiment to test his theory. He and On-Kok Chang (Keizer & Chang, 1987) studied the nonequilibrium electromotive force in a continuously stirred tank reactor with inflows of Fe^{2+}, Fe^{3+} and peroxydisulfate, $S_2O_8^{2-}$. Maximum corrections to local equilibrium of a few millivolts were observed. While not large, the results were conclusive.

IV. Amplification of Noise by Chaos

Chaos in classical physical systems is manifested by the extreme sensitivity of phase space trajectories to initial conditions. Two initially adjacent phase space points give rise to rapidly separating trajectories in a chaotic system. When this behavior is averaged over the entire available phase space, a global Lyapunov exponent can be determined. This exponent determines the rate of trajectory separation, on the average. Put another way, whenever the largest Lyapunov exponent is positive, the system is said to be chaotic (Ruell, 1989).

Every real physical system (as opposed to mathematical models) possesses intrinsic thermo-molecular fluctuations. This "noise" is unavoidable. It provides the system with an intrinsic mechanism for testing its own stability and for testing for chaos. Fluctuations nucleate phase transitions and they also nucleate the transitions from one kind of driven state to another in open systems. For example, in the Rayleigh-Benard system (Chandrasekhar, 1961), the transition from steady heat conduction to convection at the threshold for transition is nucleated by fluctuations. These phenomena strongly suggest that fluctuations play a significant role in chaotic systems as well.

The fluctuations are incessantly testing the system for a positive Lyapunov exponent. In addition, chaos amplifies the fluctuations (Fox & Keizer, 1990; Fox & Keizer, 1991). In fact, it may be shown (Fox, 1990) that as a system makes the transition from non-chaotic motion to chaotic motion, the covariances of the fluctuations initially grows exponentially and the growth rate is twice the largest local Lyapunov exponent. The qualifier, "local", refers to the fact that the exponential growth is eventually saturated by nonlinear effects and does not permit the system to necessarily explore all of the available phase space. Thus the exponential growth rate depends on where in phase space the exponentiation begins, hence local Lyapunov exponent rather than global Lyapunov exponent.

Several consequences of this effect are noteworthy. For one, fractal attractors (Ruell, 1989) occurring in mathematical models are smoothed out at some level of resolution by the chaotically amplified noise. By studying the Lorenz model (Keizer et al., 1993), it was shown that this effect could even reach the macroscopic level of resolution. In this example, a thousand fold amplification of the noise was observed and it caused the attractor to be smoothed at about the one percent level of resolution. By studying master equation models for chemical reactions, Kapral and Wu (Wu & Kapral, 1993; Wu & Kapral, 1994a; Wu & Kapral, 1994b; Kapral & Wu, 1996) showed that the amplification of fluctuations in some parameter regimes could invalidate the mass action laws at the deterministic level of description. Others (Wang & Li, 1998; Wang & Xin, 1997) have found similar results.

These same ideas lead to a novel approach to quantum chaology (Fox, 1990; Fox & Elston, 1994a; Fox & Elston, 1994b). Through the use of Husimi-Wigner distributions, quantum-classical correspondence can be achieved and quantum time evolution can be viewed as classical time evolution with an intrinsic quantum fluctuation. Thus, for a classically chaotic system treated quantum mechanically, the growth rate of the quantum covariances can be shown to be initially exponential at a rate that is twice the corresponding classical local Lyapunov exponent. This establishes the classical Lyapunov exponent as a quantum signature of classical chaos and it also suggests the means to measuring it. An experiment testing this idea has yet to be performed.

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