

MESOSCOPIC NON-EQUILIBRIUM THERMODYNAMICS FOR THE STOCHASTIC DYNAMICS OF SMALL-SCALE SYSTEMS

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ABSTRACT

We show how to extend the use of thermodynamic concepts into the mesoscopic domain where fluctuations and nonlinearities play an important role. The theory presented: mesoscopic nonequilibrium thermodynamics, provides a new interpretation of local equilibrium that is formulated at small scales. From it one derives kinetic equations and nonlinear transport equation for the study of small-scale systems outside equilibrium.

1. INTRODUCTION

Systems in equilibrium strictly follow the laws of thermodynamics [1]. Despite the disordered motion of large numbers of molecules, the system can be characterized by a few variables accounting for average properties. Thermodynamics also applies to systems outside equilibrium, in the local equilibrium regime in which the volume elements are considered small thermodynamic systems in equilibrium. This hypothesis is fundamental in the formulation of non-equilibrium thermodynamics [2].

Non-equilibrium thermodynamics is restricted to the linear response domain in which the response of the system is linear in the perturbation exerted to remove it from equilibrium. Moreover, this theory performs a macroscopic description in terms of average values not accounting for the presence of fluctuations. Whereas the linear approximation holds for transport processes such as heat conduction and mass diffusion, even in the presence of large gradients [3], it is not appropriate for describing activated processes in which the system immediately enters the nonlinear domain. Small systems [4], such as single molecules in a thermal bath, in which fluctuations and nonlinearities can be very important, are beyond the scope of this theory.

We show that a probabilistic interpretation of non-equilibrium thermodynamics which uses the concept of local equilibrium at the mesoscale [5] sets the basis of a theory able to analyze irreversible processes in the presence of fluctuations. The theory (Mesoscopic Non-equilibrium Thermodynamics [6], [7]) obtains the Fokker-Planck equation as a diffusion equation for the probability and the nonlinear relationships between activation rates and proper affinities of activated processes. The situations that can be studied with this formalism include, among others, slow relaxation processes, barrier crossing dynamics, chemical and biochemical reactions (see Fig. 1), entropic transport, active transport, dissipative self-assembly and single molecules and molecular motors [7].

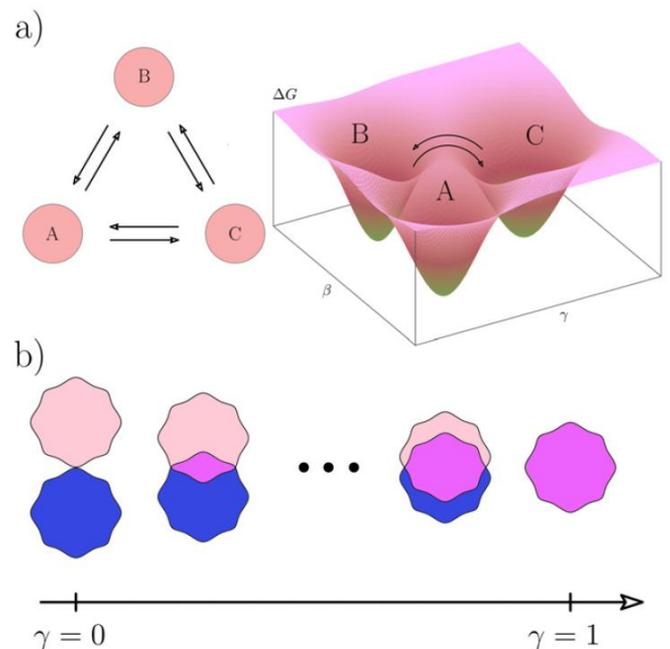


Figure 1: A chemical reaction can be treated as a diffusion process through a potential barrier that separates the initial and final states of the reaction which correspond to the minima of the potential. (a) Transformations of the molecules of a biochemical cycle viewed as a diffusion process in a free energy landscape. The configurations are described by means of two reaction coordinates γ and β . (b) In each reaction, the molecular structure of a substance transforms progressively until it reaches its final conformation.

These processes are, in general, nonlinear and influenced by the presence of fluctuations.

2. THERMODYNAMICS AND MESOSCOPIC DYNAMICS OF SMALL-SCALE SYSTEMS

A reduction of the observational time and length scales of a system usually implies an increase in the number of degrees of freedom which have not yet equilibrated and that therefore exert an influence in the overall dynamics of the system. The nonequilibrated degrees of freedom could be the velocity of a particle, the orientation of a spin, the size of a macromolecule or any coordinate or order parameter whose values define the state of the system in a phase space. The will be denoted by means of the set of coordinates γ ($\equiv \{\gamma_i\}$).

At the mesoscopic level, the characterization of the state of the system is performed through the knowledge of the probability density . The statistical expression of the entropy of the system in terms of this probability can be expressed by the Gibbs entropy postulate [2, 6]

$$S = S_{eq} - k_B \int P(\gamma, t) \ln \frac{P(\gamma, t)}{P_{eq}(\gamma)} d\gamma, \quad (1)$$

where S_{eq} denotes the entropy when the degrees of freedom γ are in equilibrium. The equilibrium probability density $P_{eq}(\gamma)$ can be related to the minimum reversible work required to create that state [4] through the expression

$$P_{eq} \sim \exp\left(\frac{-\Delta W(\gamma)}{k_B T}\right) \quad (2)$$

Here k_B is Boltzmann's constant, and T is the temperature of the heat bath. The minimum work can in general be expressed as

$$\Delta W = y\Delta Y \quad (3)$$

where y is an intensive parameter and Y its conjugated extensive variable. This general form stands for mechanical, electrical, magnetic, surface work, etc., performed on the system [4].

The expression of the minimum reversible work (3) reduces to the different thermodynamic potentials. For instance, for the case of constant temperature, volume and number of particles, the minimum work coincides with the Helmholtz free energy. The statistical mechanics definition of the entropy is therefore crucial to connect thermodynamics with the mesoscopic description in terms of the probability distribution $P(\gamma, t)$.

The dynamics of the mesoscopic degrees of freedom can be analyzed from the statistical mechanics definition of the entropy. Taking variations in Eq. (1), one obtains

$$\delta S = -k_B \int \delta P(\gamma, t) \ln \frac{P(\gamma, t)}{P_{eq}(\gamma)} d\gamma. \quad (4)$$

Conservation of the probability density in γ -space implies that it obeys the continuity equation

$$\frac{\partial P}{\partial t} = -\frac{\partial J}{\partial \gamma}, \quad (5)$$

where $J(\gamma, t)$ is a current in the space of mesoscopic coordinates.

To derive the expression of this current, we take the time derivative in equation (4) and use the continuity equation (5) to eliminate the probability time derivative. After a partial integration, one then arrives at the expression of the mesoscopic entropy production [6]

$$\sigma = -k_B \int J(\gamma, t) \frac{\partial}{\partial \gamma} \left(\ln \frac{P(\gamma, t)}{P_{eq}(\gamma)} \right) d\gamma, \quad (6)$$

This quantity expresses in the form of current-force pairs, the latter being the gradients in the space of mesoscopic variables. We will now assume a linear dependence between current and force and establish the linear relationship

$$J(\gamma, t) = -k_B L(\gamma, P(\gamma)) \frac{\partial}{\partial \gamma} \left(\ln \frac{P(\gamma, t)}{P_{eq}(\gamma)} \right), \quad (7)$$

where $L(\gamma, P(\gamma))$ is an Onsager coefficient [2], which in general depends on the probability $P(\gamma)$ interpreted as a state variable in the thermodynamic sense and on the mesoscopic coordinates γ .

The kinetic equation follows by substituting Eq. (7) into the continuity equation (5):

$$\frac{\partial P}{\partial t} = \frac{\partial}{\partial \gamma} \left(D P_{eq} \frac{\partial P}{\partial \gamma} \right), \quad (8)$$

where the diffusion coefficient is defined as

$$D(\gamma) \equiv \frac{k_B L(\gamma, P)}{P}. \quad (9)$$

This equation, which in view of Eq. (2) can also be written as

$$\frac{\partial P}{\partial t} = \frac{\partial}{\partial \gamma} \left(D \frac{\partial P}{\partial \gamma} + \frac{D}{k_B T} \frac{\partial \Delta W}{\partial \gamma} P \right), \quad (10)$$

is the Fokker-Planck equation for the evolution of the probability density in γ -space.

Under the conditions for which the minimum work is given by the Gibbs free energy G , $\Delta W \equiv \Delta G = \Delta H - T\Delta S$, where H is the enthalpy, this equation transforms into the Fokker-Planck equation for a system in the presence of a free energy barrier:

$$\frac{\partial P}{\partial t} = \frac{\partial}{\partial \gamma} \cdot \left(D \frac{\partial P}{\partial \gamma} + \frac{D}{k_B T} \frac{\partial \Delta G}{\partial \gamma} P \right). \quad (11)$$

A particularly interesting situation which will be discussed in more detail in Section 3, is the case of a purely entropic barrier, often encountered in soft-condensed matter and biophysics.

Mesoscopic nonequilibrium thermodynamics provides a general formalism able to analyze the dynamics of systems away from equilibrium from the knowledge of the equilibrium probability. In this way, by knowing the equilibrium thermodynamic potential of a system, one could derive the kinetic equation.

The mesoscopic entropy production can also be obtained from a generalized chemical potential that account for the additional mesoscopic variables. We may then assume that the evolution of these degrees of freedom is described by a diffusion process and formulate the corresponding Gibbs equation

$$\delta S = -\frac{1}{T} \int \mu(\gamma) \delta P(\gamma, t) d\gamma, \quad (12)$$

which resembles the corresponding law proposed in nonequilibrium thermodynamics for a diffusion process in terms of the mass density of particles. Here $\mu(\gamma)$ plays the role of a generalized chemical potential conjugated to the distribution function $P(\gamma, t)$. Comparison of the Gibbs equation (12) with Eq. (4), where the variations of the equilibrium entropy are given by

$$\delta S_{eq} = -\frac{1}{T} \int \mu_{eq} \delta P(\gamma, t) d\gamma, \quad (13)$$

and μ_{eq} is the value of the chemical potential at equilibrium, yields the expression of the generalized chemical potential

$$\mu(\gamma, t) = k_B T \ln \frac{P(\gamma, t)}{P_{eq}(\gamma)} + \mu_{eq}, \quad (14)$$

or alternatively, using Eq. (2),

$$\mu(\gamma, t) = k_B T \ln P(\gamma, t) + \Delta W. \quad (15)$$

In this reformulation, the ‘‘thermodynamic force’’ driving this general diffusion process is $T^{-1} \partial \mu / \partial \gamma$, and the entropy production is given by

$$\sigma = -\frac{1}{T} \int J \frac{\partial \mu}{\partial \gamma} d\gamma \quad (16)$$

This expression coincides with the entropy production of a diffusion process over a potential landscape in the space of the mesoscopic coordinates. This landscape is conformed by the values of the equilibrium energy associated to each configuration γ . The treatment of a diffusion process in the framework of nonequilibrium thermodynamics can then be extended to the case in which the relevant quantity is a probability density instead of a mass density. This fact shows the close connection between entropy and stochastic dynamics.

3. AN EXAMPLE: ACTIVATED PROCESSES

In this Section, we will apply our general formalism to the study of the kinetics of activated processes. We will show how

the Fokker-Planck equation can be obtained from a diffusion process of the probability compatible with the statistical formulation of the second law. We will also illustrate how to derive the nonlinear equations for the activation rate in terms of the affinity of the process.

Activated processes are frequently modeled by a particle crossing a free energy barrier that separates two well-differentiated states located at the minima at each side of the barrier. Processes such as chemical reactions, adsorption, nucleation, thermal emission in semiconductors, and active transport through biological membranes, share these features and, therefore, are generically referred to as activated processes.

These processes are essentially different from the linear transport processes described by nonequilibrium thermodynamics. The latter constitute the instantaneous response to an applied external force or gradient and may take place even at very low values of the force. Since activated processes need of a minimum of energy to proceed, the regime in which they may be observed is essentially nonlinear. This difference becomes even more evident when we contrast the form of Fourier, Fick, or Ohm laws, in which the corresponding currents are proportional to the conjugated thermodynamic forces or gradients, with the exponential Arrhenius laws for the rates in activated processes.

To better illustrate this point, let us consider a general process for which a system passes from state 1 to state 2 via activation. Instances of this process can be a chemical reaction in which a substance transforms into another, an adsorption process in which the adsorbing particle goes from the physisorbed to the chemisorbed state, or a nucleation process in which the metastable liquid transforms into a crystal phase. Nonequilibrium thermodynamics describes the process only in terms of the initial and final positions, obtaining a linear behaviour of the current in terms of the affinity which only agrees with the law of mass action for small values of the affinity. If we consider the process at shorter time scales, the state of the system instead of jumping from 1 to 2, progressively transforms by passing through successive molecular configurations. These configurations can be characterized by a reaction coordinate γ . At these time scales, one may assume that the reaction coordinate undergoes a diffusion process through a potential barrier separating the initial from the final states (see Fig. 1).

At the time scales of interest, the system is mostly found in the states 1 and 2, which correspond to the minima at γ_1 and γ_2 , respectively. In the quasi-stationary limit, when the energy barrier is much higher than the thermal energy and intra-well relaxation has already taken place, the probability distribution is strongly peaked at these values and almost zero everywhere else. Under these conditions, the Fokker-Planck description, leads to a kinetic equation in which the net reaction rate satisfies the mass action law.

The current obtained from the mesoscopic entropy production (16) can be rewritten in terms of the local fugacity defined along the reaction coordinate $z(\gamma) \equiv \exp \mu(\gamma) / k_B T$ as

$$J = -k_B L \frac{1}{z} \frac{\partial z}{\partial \gamma}, \quad (17)$$

which can be expressed as

$$J = -D \frac{\partial z}{\partial \gamma}, \quad (18)$$

where $D = k_B L / z$ is the diffusion coefficient. We now assume that D is constant and integrate from 1 to 2 to obtain the nonlinear kinetic law for the averaged current

$$\bar{J} \equiv \int_1^2 J d\gamma = -D(z_2 - z_1) = -D \left(\exp \frac{\mu_2}{k_B T} - \exp \frac{\mu_1}{k_B T} \right). \quad (19)$$

This equation can also be expressed as

$$\bar{J} = J_0 \left(1 - e^{A/k_B T} \right),$$

where \bar{J} is the averaged rate, $J_0 = D \exp(\mu_1/k_B T)$ and $A = \mu_1 - \mu_2$ is the corresponding affinity. We have then shown that a Fokker-Planck equation, linear in probabilities and in the gradient of $\mu[\gamma, P(\gamma)]$, accounts for a non-linear dependence in the affinity. The scheme presented has been successfully applied to different classical activated processes, like chemical reactions, nucleation, active transport in ion channels, and molecular motors, to obtain the corresponding kinetic laws.

4. CONCLUSIONS

In this article, we have shown how to extend the use of thermodynamic concepts into the mesoscopic domain where fluctuations and nonlinearities play an important role. The probabilistic interpretation of thermodynamics together with

probability conservation laws can be used to obtain kinetic equations for the mesoscopic degrees of freedom.

The approach we have presented starts from the mesoscopic equilibrium behavior and adds all the dynamic details compatible with the second principle of thermodynamics and with the conservation laws and symmetries of the system. From the knowledge of the equilibrium properties of a system, it is straightforward to obtain Fokker-Planck equations for its dynamics. The coefficients entering the dynamic equations can be obtained from experiments or microscopic theories.

We have shown explicitly the applicability of the mesoscopic nonequilibrium thermodynamics to study the kinetics of activated processes showing that the formulation of local equilibrium at small scales leads to the nonlinear kinetic equations that govern those processes.

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