

On the Theory of Fluctuations in Continuum Systems

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The probability of occurrence of fluctuations around nonequilibrium steady states is discussed from a kinetic viewpoint. It is shown that in a large class of continuous media it is possible to extend the thermodynamic theory of fluctuations, provided one uses suitable steady-state parameters rather than equilibrium quantities.

KEY WORDS: Fluctuations; stochastic processes; continuous media; master equation

1. INTRODUCTION

In a previous paper (Ref. 1, hereafter referred to as I), we presented an analysis of the fluctuation properties of open thermodynamic systems characterized by a discrete set of variables. Using a master-equation approach, we have been able to show that the results of the equilibrium theory of fluctuations can be generalized immediately to the problem of fluctuations around states arbitrarily far from equilibrium, provided one uses suitable asymptotic approximations (or, alternatively, provided the limit of relatively small fluctuations is taken). Essential for the derivation of the results has been the use of an assumption that we have presented in I as the decoupling assumption. Its content is as follows. The concept of a steady nonequilibrium state corresponds to an approximation valid when the characteristic time scales of an overall isolated system separate into very long ones (such as those determining the time evolution of the external reservoirs) and short ones (determining the evolution of a nonisolated system in contact with the reservoirs). It may thus be expected that the internal state of the system does not influence directly the state of the reservoirs. This is the decoupling assumption; in I we have shown that it permits one to deduce a closed master equation for the evolution of the system, in which the state variables of the reservoirs appear as parameters.

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At first sight, it would seem that the methods and the results of I are limited to the case of discrete systems, for which the master equation is an ordinary differential-difference equation. It is the purpose of the present note to discuss an extension of the results to a typical continuum problem, for example, the problem of internal energy fluctuations around nonequilibrium states. Again the master equation approach will be used throughout. The problem will be approached in two stages. In Section 2, we consider a model corresponding to a Knudsen gas in contact with two heat and matter reservoirs. In this case, the interactions between system and reservoirs are easily accounted for and the problem admits a general solution. In the limit of small fluctuations, the result is an Einsteinlike formula as in I. In Section 3 we consider the problem of energy fluctuations in a strongly coupled system. To simplify the analysis, we limit ourselves from the very start to the small-fluctuation case. We are then able to derive generalized Einstein formulae as in Section 2. Let us recall that in the case of continuous media the Einstein formula for energy fluctuations leads to^(2,3)

$$\rho(E) \sim \exp \left[- \int \frac{(\Delta E)^2}{C_v k T^2(\mathbf{r})} d\mathbf{v} \right] \quad (1)$$

where ρ is the probability function, $T(\mathbf{r})$ is the local temperature and C_v the heat capacity, and $d\mathbf{v}$ refers to a volume integration.

Some comments and deductions are presented in Section 4.

2. ENERGY FLUCTUATIONS: THE KNUDSEN GAS MODEL

We first consider the limiting case of a system in contact with two heat reservoirs at temperatures T_1 and T_2 . The ratio $(T_2 - T_1)/T_2$ can be made large, thus accounting for arbitrary quasistationary states far from equilibrium. Our problem is to describe the energy fluctuations around such steady states. To this end, we set up a master equation for the probability function $\rho(E_1, E_2, E, t)$ for having, at time t , the energy values E_1, E_2 for the two reservoirs and an energy value E for the system. As in I, we again adopt a Markovian stochastic approximation. It will also be convenient to discuss the energy fluctuations at constant pressure.

The principal difficulty encountered in writing such a master equation lies in the explicit form of the transition probabilities which express the efficiency of energy transfer between system and reservoirs. These transition probabilities depend ultimately upon the forces of interaction between system and reservoirs. In this section, we discuss a model for these interactions which corresponds to a Knudsen gas. The reason for choosing this model is the following. Let $P(E + \Delta E)$ be the transition probability for going from a state of energy $E + \Delta E$ to a state E . In a Knudsen gas, the intermolecular interactions are negligible and the transfer of energy occurs always through a transport of mass. It is known from thermodynamics⁽²⁾ that the energy carried in such a process is equal to

$$\Delta E = nkT \quad (2)$$

n being the number of molecules transported between system and reservoir. Therefore, by adopting the Knudsen gas model, we automatically have the means to specify the energy variations in a transition due to a system-reservoir interaction. Finally, the form of the function $P(E)$ itself is implied by the fact that we deal with systems of noninteracting particles. It follows that

$$P(E) = KE \tag{3}$$

K being a suitable proportionality factor depending upon the structure of the system and of the reservoirs.

We are now able to write the equation for the probability function $\rho(E_1, E_2, E)$. Using the methods of Ref. 1 and the assumption of stochastic independence between the effects of the two reservoirs upon the system, it is straightforward to obtain

$$\begin{aligned} \frac{\partial}{\partial t} \rho(E_1, E_2, E) = & K[(E_1 + \Delta E) \rho(E_1 + \Delta E, E_2, E - \Delta E) - E_1 \rho(E_1, E_2, E)] \\ & + K[(E + \Delta E) \rho(E_1 - \Delta E, E_2, E + \Delta E) - E \rho(E_1, E_2, E)] \\ & + K[(E + \Delta E) \rho(E_1, E + \Delta E, E_2 - \Delta E) - E \rho(E_1, E_2, E)] \\ & + K[(E_2 + \Delta E) \rho(E_1, E_2 + \Delta E, E - \Delta E) - E_2 \rho(E_1, E_2, E)] \end{aligned} \tag{4}$$

We have used the additional assumption that the energy transfer ΔE as given by (2) is the same for all transitions.

It is convenient to define the new set of variables

$$\begin{aligned} \tilde{E}_i &= E_i/\Delta E \quad (i = 1, 2) \\ \tilde{E} &= E/\Delta E \end{aligned} \tag{5}$$

Equation (4) then transforms into a finite difference form which is identical to the form arising in the chemical kinetical problems discussed in I. By transforming to the generating function space^(1,4) and by invoking the decoupling assumption introduced in I, we finally obtain the solution

$$\rho = [\exp(-\tilde{E}_{st})] \frac{\tilde{E}_{st}^{\tilde{E}}}{\tilde{E}!} \tag{6}$$

where \tilde{E}_{st} is the average steady-state value of \tilde{E} :

$$\tilde{E}_{st} = N_s(\tilde{E}_1 + \tilde{E}_2)/2N_r \tag{7}$$

and N_s and N_r are the average numbers of particles in the system and in the reservoir, respectively.

In the limit of small fluctuations, Eq. (6) reduces to

$$\rho \sim \exp[-(E - \bar{E})^2/2Ek\bar{T}] \tag{8}$$

where

$$\bar{T} = (T_1 + T_2)/2 \quad (8a)$$

For a Knudsen gas,

$$E = N_s k \bar{T} = C_v \bar{T}$$

therefore,

$$\rho \sim \exp[-(\Delta E)^2/2C_v k \bar{T}^2] \quad (9)$$

This result is the limit of the thermodynamic formula (1) corresponding to two reservoirs rather than that of a continuous distribution of temperature. In the same way as in I, the difference between Eqs. (9) and (1) is that, in Eq. (9), the parameter \bar{T} refers to the *steady-state temperature distribution* rather than to the equilibrium value appearing in the usual thermodynamic result.

The generalization to the case of an arbitrary number of reservoirs is straightforward and will not be reproduced here. The result is again in agreement with the classical thermodynamic formulae of fluctuation theory.

3. ENERGY FLUCTUATION IN STRONGLY COUPLED SYSTEMS

In this section, we present a generalization of the treatment of Section 2 to systems whose coupling with reservoirs cannot be satisfactorily considered in the simple Knudsen limit. We again consider a system in contact with two heat reservoirs. In agreement with the Markovian stochastic approximation, the evolution of the probability density function $\rho(E, t)$ will be given by the Smoluchowski equation⁽⁴⁾

$$\rho(E, t + \Delta t) = \int dE' q_1(E'/E, \Delta t) \rho(E', t) + \int dE'' q_2(E''/E, \Delta t) \rho(E'', t) \quad (10)$$

where $q_i(E'/E, \Delta t)$ are the probabilities for transitions leading from a state of energy E to a state of energy E' due to the interactions between the system and the i th reservoir.

Because of the complicated structure of Eq. (10) in the general case, we only discuss here the limit of small energy changes during a transition:

$$(E - E')/E \ll 1, \quad (E - E'')/E \ll 1 \quad (11)$$

These assumptions do not confine the system close to equilibrium (see Lax⁽⁵⁾).

Upon expanding Eq. (10) in powers of the two smallness parameters introduced in (11) and retaining the first nontrivial terms, we finally obtain a Fokker-Planck equation with nonlinear coefficients:^(4,5)

$$\frac{\partial \rho}{\partial t} = - \frac{\partial}{\partial E} A_1(E) \rho(E) - \frac{\partial}{\partial E} A_2(E) \rho(E) + \frac{\partial^2}{\partial E^2} D_1(E) \rho(E) + \frac{\partial^2}{\partial E^2} D_2(E) \rho(E) \quad (12)$$

where we have defined

$$A_i(E) = (1/\Delta t) \int dE' q_i(E/E', \Delta t)(E' - E) \quad (13a)$$

$$D_i(E) = (1/2 \Delta t) \int dE' q_i(E/E', \Delta t)(E' - E)^2 \quad (13b)$$

We also note the usual normalization conditions

$$\sum_i \int dE' q_i(E/E', \Delta t) = 1 \quad (14)$$

In this section, we only study the limit of Eq. (12) corresponding to small fluctuations:

$$(E - \bar{E})/E \ll 1 \quad (15)$$

where \bar{E} is the average value of the energy in the system. Again assumption (15) does not imply close to equilibrium conditions. Upon expanding Eq. (12) and retaining the first nontrivial terms, we obtain an ordinary Fokker-Planck equation with linear coefficients. This equation may then be used to calculate the mean-square deviation of the energy fluctuations. The final result is

$$\langle (E - \bar{E})^2 \rangle_{\text{av}} = \frac{D_1(\bar{E}) + D_2(\bar{E})}{\mathcal{A}_1 + \mathcal{A}_2 - 1} \quad (16)$$

where we define

$$\mathcal{A}_i = - \int dE' (\partial q_i / \partial E)_{\bar{E}} (E' - \bar{E}) \quad (17)$$

At this point, it is necessary to specify the function q_i somewhat more. Let $\sigma(E)$ be the density of states function of the system. The transition probability q_i assumes then the form

$$q_i = \delta(E - E')(1 - l_i \Delta t) + W_{E,E'}^i \Delta t \quad (18a)$$

with

$$W_{E,E'} = t_{E,E'}^i \sigma_i(E') \quad (18b)$$

$t_{E,E'}$ being proportional to the cross section for an $E \rightarrow E'$ transition and l being a constant. Equation (17) can be written as

$$\mathcal{A}_i = - \int dE' (\partial t_{E,E'}^i / \partial \bar{E}) \sigma_i(E')(E' - \bar{E}) \quad (19)$$

We now introduce the following fundamental, physically reasonable assumption. We consider that $t_{E,E'}$ as a function of \bar{E} and E' depends upon the energy differences $\bar{E} - E'$ only:

$$\partial t_{E,E'} / \partial \bar{E} = - \partial t_{E,E'} / \partial E' \quad (20)$$

Using Eq. (20), expression (19) reduces to

$$\sum_i \mathcal{A}_i = \sum_i \int dE' (E' - \bar{E}) t_{\bar{E}, E'}^i \sigma_i(E') \partial[\ln \sigma_i(E')]/\partial E' + 1 \quad (21)$$

On the other hand, it is well known that⁽⁸⁾

$$\partial[\ln \sigma_i(E)]/\partial E = 1/kT_i(E) \quad (22)$$

since the system is at equilibrium with each of the individual reservoirs along the boundary of thermal contact.

Upon expanding $T_i(E)$ around $T_i(\bar{E})$ and retaining terms of order of $(E - \bar{E})^2$, we obtain (cf. Ref. 3)

$$(E - \bar{E})^2 = \frac{D_1(\bar{E}) + D_2(\bar{E})}{(A_1/kT_1) + (A_2/kT_2) + [D_1(\bar{E})/C_v(T_1) T_1^2] + [D_2(\bar{E})/C_v(T_2) T_2^2]} \quad (23)$$

Equation (23) expresses the fluctuations around a quasistationary state arbitrarily far from equilibrium.

Unfortunately, the complicated structure of (23) does not permit a simple solution in terms of thermodynamic quantities. However, if we confine the system to steady states close to equilibrium, it is again possible to recover the thermodynamic result (1). Let us set

$$T_1 = \bar{T} - \Delta T, \quad T_2 = \bar{T} + \Delta T$$

where \bar{T} is the temperature of the system. For states close to equilibrium, $\Delta T/\bar{T}$ is small. Upon expanding (23) around \bar{T} and retaining terms of order $\Delta T/\bar{T}$ only, we obtain

$$(E - \bar{E})^2 = \frac{D_1(\bar{E}) + D_2(\bar{E})}{\frac{1}{k\bar{T}} [A_1(\bar{E}) + A_2(\bar{E})] + \frac{1}{kC_v\bar{T}^2} [D_1(\bar{E}) + D_2(\bar{E})]} + \frac{\Delta T}{\bar{T}^2} [A_1(\bar{E}) - A_2(\bar{E})] + \frac{\Delta T}{C_v\bar{T}^2} [D_1(\bar{E}) - D_2(\bar{E})] \left(\frac{\partial \ln C_v}{\partial T} + \frac{2}{\bar{T}} \right) \quad (24)$$

It is easy to show that $A_1 - A_2$ and $D_1 - D_2$ are of order ΔT , and therefore the corresponding terms in (24) are of order ΔT^2 and thus negligible.

Moreover, it can be shown that, if one computes the total energy flux in the system using Eq. (12) and if one requires it to vanish at the steady state (as it should), one obtains the condition

$$A_1(\bar{E}) + A_2(\bar{E}) = 0 \quad (25)$$

Equation (24) reduces to

$$\langle (E - \bar{E})^2 \rangle_{av} = k\bar{T}^2 C_v \quad (26)$$

where \bar{T} is the average nonequilibrium temperature in the system. Under the same conditions, the solution of Eq. (12) reads

$$\rho(E) \sim \exp[-(E - \bar{E})^2/2C_v k\bar{T}^2] \quad (27)$$

We have therefore obtained a formula similar to the thermodynamic result (1). Again the generalization of this result to a system in contact with an arbitrary number of reservoirs is straightforward. It should be mentioned that a study of nonequilibrium stationary states close to equilibrium using a stochastic interaction model with arbitrary external reservoirs has been made by Lebowitz and Bergmann.⁽⁶⁾ These authors, however, deal with the transport properties of the system rather than with the fluctuations of thermodynamic quantities.

4. DISCUSSION

In this paper, we have followed a master-equation approach to discuss the thermodynamic energy fluctuations of a system in contact with a number of energy reservoirs at different temperatures. The main result we have derived is that the classical equilibrium fluctuation theory can be immediately extrapolated to arbitrary far-from-equilibrium situations, at least for the Knudsen gas model. For strongly coupled systems, we have only been able to show its validity for steady states close to equilibrium.

An alternative (nonthermodynamic) way of formulating the problem of fluctuation of energy or temperature would be to adopt the methods of stochastic differential equations and consider the Fourier heat transfer equation as stochastic.⁽⁷⁾ More precisely, consider a system in contact with two heat reservoirs. The steady-state Fourier equation reads

$$\nabla^2 T = 0 \quad (28)$$

This equation can be solved with stochastic boundary conditions. The most natural conditions one can set correspond to a temperature distribution of the reservoirs given by the equilibrium formula (1) and to the absence of correlations between the two reservoirs. The surprising result is then that the probability distribution for temperature (or for energy) fluctuations inside the system does not reduce to one of the thermodynamic forms derived in Section 2 or 3. Conversely, we have shown that, in order to obtain the thermodynamic result for the temperature fluctuations in the system, it is necessary to introduce a distribution of the external reservoirs involving complicated cross-correlations. We may conclude, therefore, that the stochastic-differential-equation approach to fluctuations has no direct relevance to the problem of *thermodynamic* fluctuations.

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