

STUDIES OF THERMAL FLUCTUATIONS IN NONEQUILIBRIUM SYSTEMS BY MONTE CARLO COMPUTER SIMULATIONS

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In recent years, there has been much interest in the nature of the fluctuations in nonequilibrium systems [1]. Most of the work in this field has consisted of studying the composition fluctuations for a given system through the Master Equation, the Fokker-Planck Equation or a Stochastic Differential Equation. Recently, these methods have been applied to the study of thermal systems by Nicolis, Baras, and Malek Mansour [2]. In this paper, we review their analysis of the two reservoir model. We discuss a computer simulation which has been developed to study this system and present a confirmation of their thermal fluctuation predictions.

1. ANALYSIS

In this section, we essentially review the analysis for the two reservoir model presented in Nicolis, Baras, and Malek Mansour [2]. The two reservoir model consists of a system connected to two reservoirs by Knudsen apertures. We assume that the system interacts with the two reservoirs, exchanging both particles and energy. We assume that the system is spatially homogeneous and that the time scale for thermalization is small compared to the time scale for the flow so that the system is almost always in a state of thermal equilibrium. With this condition we may define a temperature analogous to the equilibrium temperature and may assume that the velocity distribution is Maxwell-Boltzmann. If we assume Knudsen flow through a hole of cross-section, σ , then we

may write the macroscopic equations for the number density n , and the energy density e ,

$$\frac{dn}{dt} = \frac{\sigma}{V} \sqrt{\frac{k}{2\pi m}} \left[n_1 T_1^{1/2} + n_2 T_2^{1/2} - 2n\bar{T}^{1/2} \right] \quad (1)$$

$$\frac{de}{dt} = \frac{2\sigma}{V} \sqrt{\frac{k^3}{2\pi m}} \left[n_1 T_1^{3/2} + n_2 T_2^{3/2} - 2n\bar{T}^{3/2} \right]$$

where \bar{T} is the temperature, m the molecular mass, V the system volume, and k is Boltzmann's constant. We solve Eq. (1) for the steady-state number density and temperature, n_s and \bar{T}_s ,

$$\bar{T}_s = \frac{n_1 T_1^{3/2} + n_2 T_2^{3/2}}{n_1 T_1^{1/2} + n_2 T_2^{1/2}} \quad n_s = \frac{n_1 T_1^{1/2} + n_2 T_2^{1/2}}{2\bar{T}_s^{1/2}} \quad (2)$$

In order to write the Master Equation for the two reservoir system we need the transition rate between the state (particle number N , total energy E) and the state $(N+r, E+\epsilon)$. We know that the rate at which particles reach the hole is proportional to their velocity, and that we have a Maxwell-Boltzmann velocity distribution. From this we may write that the transition rate, $W(N, E, N+r, E+\epsilon)$, is,

$$W(N, E, N+r, E+\epsilon) = \frac{4\pi\sigma}{m^2 V} \left(\frac{m}{2\pi k} \right)^{3/2} |\epsilon| \begin{cases} N_1 T_1^{-3/2} \exp(-\epsilon/kT_1) & r=1, \epsilon>0 \\ N_2 T_2^{-3/2} \exp(-\epsilon/kT_2) & \\ 2NT^{-3/2} \exp(\epsilon/kT) & r=-1, \epsilon<0 \end{cases} \quad (3)$$

where T is the fluctuating temperature and so we may write the Master Equation as,

$$\frac{d}{dt} P(N, E) = \sum_{r=-1}^1 \int_{-\infty}^{\infty} d\epsilon \begin{aligned} & W(N-r, E-\epsilon, N, E) P(N-r, E-\epsilon) \\ & - W(N, E, N+r, E+\epsilon) P(N, E) \end{aligned} \quad (4)$$

We now wish to take the thermodynamic limit of our Master Equation. In this limit the realizations for our Markov process tend to continuous paths. If the first two truncated differential moments exist then the Markov process is said to be a diffusion

process. The general definition for the (l,k) th differential moment is,

$$A_{l,k}(n,e) \equiv \sum_{r=-1}^1 \int_{-\infty}^{\infty} d\epsilon \left(\frac{r}{V}\right)^l \left(\frac{\epsilon}{V}\right)^k W(N,E,N+r,E+\epsilon) \quad (5)$$

We define for convenience f and G^2 as,

$$f \equiv \begin{pmatrix} A_{1,0} \\ A_{0,1} \end{pmatrix} \quad G^2 \equiv V \begin{pmatrix} A_{2,0} & A_{1,1} \\ A_{1,1} & A_{0,2} \end{pmatrix} \quad (6)$$

It can be demonstrated that under some weak conditions of f and G^2 the transition probability density obeys a Fokker-Planck Equation of the form,

$$\partial_t p(n,e) = -(\partial_n \partial_e) (fp) + \frac{1}{2V} (\partial_n \partial_e) \left[(\partial_n \partial_e) (G^2 p) \right]^T \quad (7)$$

Horsthemke and Brenig [3] stress a very important point about this analysis; since a continuous Markov process is completely characterized by its first two differential moments it is unnecessary to consider the asymptotic behavior of the higher order differential moments.

At this point, we assert that from physical considerations we can assume that the state-dependent diffusion term, $G(n,e)$, can be replaced by the state-independent diffusion, $G(n_s, e_s)$, since the system, in the thermodynamic limit, will almost always be near the steady state. Malek Mansour, et.al. [4] demonstrated that this replacement was valid for a large class of chemical systems. If we switch from the independent variables (n,e) to (n,T) , integrate the Fokker-Planck Equation, expanding f about the steady state, we obtain,

$$\langle (\delta n)^2 \rangle = n_s \left[1 - \frac{\Delta}{5} \right], \quad \langle \delta n \delta T \rangle = \frac{2}{5} \Delta, \quad \langle (\delta T)^2 \rangle = \frac{\bar{T}_s^2}{3n_s/2} \left[1 - 14\Delta/5 \right] \quad (8)$$

where

$$\Delta \equiv \frac{(\bar{T}_s - T_1)(\bar{T}_s - T_2)}{2 \bar{T}_s^2} \quad (9)$$

We notice that the departure from the equilibrium values appears quadratically and that it is most prominent for the thermal fluctuations.

II. SIMULATIONS

In developing the simulation for the two reservoir system we tried to meet two important criteria. First, the simulation had to be fast. Since we were interested in measuring fluctuations in a large system we required very accurate statistics, at least millions of events. Secondly, we tried to keep an eye towards developing simulations for the next generation of thermal fluctuation problems, those with exothermic chemistry and spatial extent.

In deciding what type of code to use, we had several frameworks to choose from. Almost immediately, we rejected using a molecular dynamics code [5] because of our first criterion; also a molecular dynamics code would contain much more detail than we were really interested in. Our second choice was to use a collisionless Monte Carlo code [6]. In this context, by a collisionless code we mean one in which the collisions in the system were not explicitly calculated but rather were assumed to always keep the system in a Maxwell-Boltzmann distribution. This would certainly meet our first criterion but we were not certain whether it would provide enough microscopic detail for more complex systems. For the two reservoir system though it was certainly adequate. A collisional Monte Carlo algorithm was our third choice [7]. It seemed to best meet our criteria, however since most such codes are concerned with flow problems and not with the careful modeling of thermal fluctuations or of sensitive chemical reactions, we had to make some modifications. In conclusion, we wrote three codes, one collisionless and two collisional Monte Carlo codes. Only the collisionless code will be discussed in any detail in this paper.

In the collisionless code, we monitor only the total number of particles and the total energy. We assume that the particles are always thermalized to a Maxwell-Boltzmann distribution by collisions in the system. In the code, three fundamental events may occur. A particle may leave the system, a particle may enter the system from reservoir 1, or one may enter from reservoir 2. We compute these rates, W , from the macroscopic equation, Eq. (1), so,

$$W_0 = 2KnT^{1/2}, \quad W_{1,2} = Kn_{1,2} T_{1,2}^{1/2}$$

$$K \equiv \frac{\sigma}{V} \sqrt{\frac{k}{2\pi m}}, \quad W_s = W_0 + W_1 + W_2 \quad (10)$$

The time till the next event, τ , is chosen in the appropriate Monte Carlo way as,

$$\tau = -\ln(R)/W_s \quad (11)$$

and R is a random number in $(0,1)$. The type of the next event, ℓ , is chosen as,

$$\sum_{i=0}^{\ell-1} W_i < RW_s < \sum_{i=0}^{\ell} W_i \quad \ell = 0, 1, 2 \quad (12)$$

All that is left is to determine the energy of the particle which enters or leaves. From the transition rate of the Master Equation, Eq. (3), we can write that the probability of a particle of energy ϵ leaving the system is,

$$P(\epsilon)d\epsilon = \frac{\epsilon}{(kT)^2} \exp(-\epsilon/kT)d\epsilon \quad (13)$$

Then we can make the appropriate Monte Carlo choice as to the particle's energy ϵ as,

$$\epsilon = -kT \ln(R_1 R_2) \quad (14)$$

A similar analysis can be done for particles entering the system. We have now entirely specified the dynamics of the process and the code simply has to successively choose an event and update the system given this event.

The collisionless Monte Carlo code has been very successful for the two reservoir system. It is small and can do ten million events in about one hour on a VAX 11/780 computer. For systems of some 500 and 1000 particles, we have made runs at several temperatures. Figure 1 summarizes our results so far for the temperature fluctuations and we are pleased at the agreement with the values predicted by Eq. (8). Though statistics were taken for the other fluctuations, the number fluctuations and the number-temperature correlations will not differ substantially from the equilibrium values and so are not conclusive.

The only results we have for the collisional Monte Carlo codes are timing comparisons with the collisionless code. In the collisional codes, the state of the system is fixed by the velocity distribution of the system. A collisional code which uses the average energy per particle to approximate the collision frequency is virtually as fast as the collisionless code when considering the number of events processed, however, the collisionless code is actually considerably faster since most of the events in the

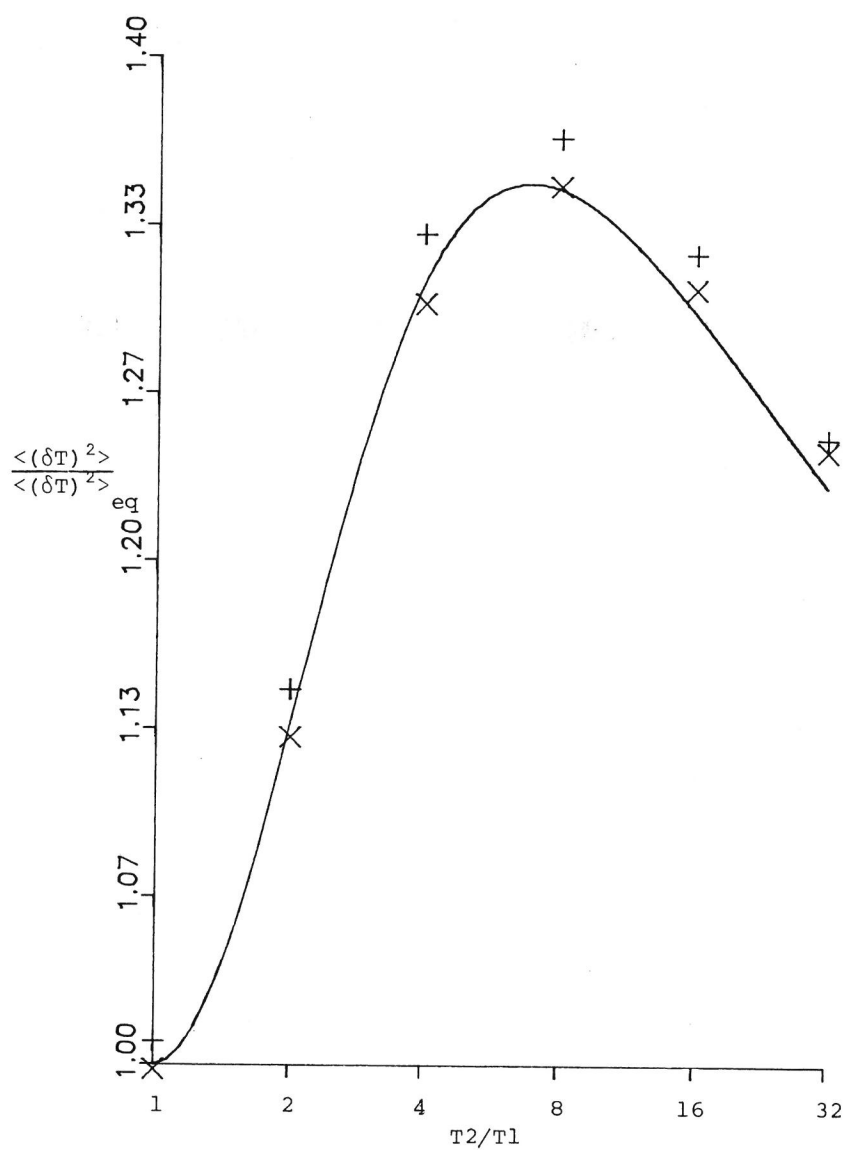


Figure 1

Thermal Fluctuations, Normalized at Equilibrium

 $N_1 = N_2$; $T_1 = 200$; NOE = Number of Events+ $N_1 = 500$, NOE = 20 MillionX $N_1 = 1000$, NOE = 40 Million

collisional code are elastic thermalizing collisions. A collisional code which computes the collision frequency exactly spends about 90-95% of its time in that calculation and is thus considerably slower than the other two codes.

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