

Deviations from the Poisson Behavior of Equilibrium Fluctuations in a Closed System

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A molecular dynamics simulation of dimer formation in an adiabatic, hard-core, square-well, dilute two-dimensional gas yields a non-Poissonian dimer number distribution. Its ratio of variance to mean deviates from unity in a manner recently predicted theoretically.

KEY WORDS : Equilibrium fluctuations ; non-Poisson behavior ; molecular dynamics ; dimer formation.

1. INTRODUCTION

Fluctuations in both equilibrium and nonequilibrium chemical systems have been recently of considerable interest.⁽¹⁻⁵⁾ The Poisson formula has been found to give an excellent description of their distribution both in and out of equilibrium in remarkably many instances. Undisputably, there are situations where one cannot expect and does not observe this simple behavior. Chemical instabilities investigated by Prigogine and his co-workers⁽²⁻⁴⁾ yield examples of that sort. Still, a first guess about the Poisson nature of equilibrium or steady-state fluctuations is very often a correct one.

It is therefore somewhat surprising that a simple chemical system can deviate from the Poisson behavior, as was recently pointed out by Van Kampen⁽⁶⁾ and Hanusse.⁽⁷⁾ They have found that in a *canonical ensemble* the conservation of the total number of atoms implies a modification of the Poisson distribution. Moreover, they have shown that these differences *do not* vanish in the limit of an infinitely large system.

Non-Poissonian behavior in a closed system was justified by Van Kampen⁽⁶⁾ via a birth-death equation for the probability distribution for numbers of chemically distinct molecules. It was also assumed there that the

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system is kept in thermal and chemical homogeneity by stirring, which was expected to destroy even the short-range correlations. These combined assumptions were found previously to lead to a non-Poissonian behavior in far-from-equilibrium systems, which, when analyzed more carefully, behave in a Poissonian fashion. Nicolis and Prigogine⁽⁴⁾ have shown that deviations from Poissonian behavior disappear when the analysis is conducted by means of a more complete birth-death equation in a phase space rather than in number space. Their conclusion has been confirmed by molecular dynamics experiments.⁽⁵⁾

Even though this failure of birth-death number space representation was detected by Nicolis and Prigogine far from equilibrium, and number space considerations of Hanusse and Van Kampen leading to the non-Poissonian predictions for fluctuations refer to the equilibrium canonical ensemble, it seems interesting to verify their conclusions by comparison with a molecular dynamics experiment. This is the purpose of this paper.

2. FLUCTUATIONS IN A CANONICAL ENSEMBLE

We shall direct our attention to the problem of dimer formation. For this Van Kampen has derived explicit formulas. He has considered the reaction



and has found that the equilibrium distribution of the number of dimers N_2 in a *canonical* ensemble is given by

$$P(N_2) = C(\Omega Z_2)^{N_2}(\Omega Z_1)^{N-2N_2}/[N_2!(N-2N_2)!] \quad (2)$$

Here, C is the normalization constant, Z_1 and Z_2 are the usual monomer and dimer partition functions, and Ω is the volume of the container in which N atoms are always present ($N_1 + 2N_2 = N$). This formula is different from the *grand canonical* prediction, which for dimers would be

$$P(N_2) = C(\Omega Z_2)^{N_2}/N_2! \quad (3)$$

and an analogous formula would hold also for monomers.

The validity of (2) can be verified by considering the Markovian gain-loss equation⁽¹⁻⁴⁾:

$$\begin{aligned} \dot{P}(N_2, N_1) = & \Omega\kappa[(N_2 + 1)(N_1 - 2)P(N_2 + 1, N_1 - 2) - N_2 N_1 P(N_2, N_1)] \\ & + \Omega\kappa'\{(N_1 + 2)(N_1 + 1)(N_1)P(N_2 - 1, N_1 + 2) \\ & - N_1(N_1 - 1)(N_1 - 2)P(N_2, N_1)\} \end{aligned} \quad (4)$$

This gain-loss equation corresponds to the actual reaction of dimer formation, Eq. (6), rather than the simplified version of it given by (1).

Probability distribution $P(N_2, N_1)$ satisfies (4) providing that constants κ and κ' are related by the law of mass action, $\kappa/\kappa' = Z_1^2/Z_2$.

Even in an infinitely large system ($N \rightarrow \infty$) the two probability distributions (2) and (3) remain different. This is best seen by comparing the variance with the average value of N_2 for both. The closed system distribution yields in the limit of large N

$$r = \langle (N_2 - \langle N_2 \rangle)^2 \rangle / \langle N_2 \rangle = [1 + 8(Z_2/Z_1^2)(N/\Omega)]^{1/2} \quad (5)$$

This ratio r is equal to unity for the Poisson distribution (3).

3. A COMPARISON WITH MOLECULAR DYNAMICS

Let us now compare predictions of the two results with a molecular dynamics (MD) experiment. We consider dimers formed in a three-body collision between hard-core, square-well particles of an imperfect gas. The chemical reaction reads



Although this reaction is different from the one considered in (1), it yields the same predictions for the equilibrium distribution of fluctuations, since the equilibrium distribution function is sensitive only to the conservation laws and not to the details of the reaction scheme. Therefore, a system simulated by means of molecular dynamics is almost the same as the one for which Eqs. (2) and (5) were derived. Almost, because the simulated system is adiabatic rather than isothermal. Moreover, the molecular dynamics program admits a possibility of creation of chemical species larger than dimers. Before we compare results of molecular dynamics with theoretical value for $\langle (N_2 - \langle N_2 \rangle)^2 \rangle / \langle N_2 \rangle$, we must ascertain that the effects of adiabaticity and the existence of clusters larger than dimers are much smaller than the effect given by (2) itself. We find it more convenient to postpone detailed discussion of these corrections to Section 4 and present now the results of the comparison between the molecular dynamics experiment and the two possible equilibrium distributions (2) and (3).

As in earlier work, we have studied a system of 100 hard-core, square-well disks in periodic boundary conditions.⁽⁸⁻¹⁰⁾ All the particles are identical, with mass $m = 6.628 \times 10^{-23}$ g, radius of the hard core $\sigma_1 = 2.98 \times 10^{-8}$ cm, radius of the outer well $\sigma_2 = 1.96\sigma_1$, and depth of the well $\epsilon = 2.305 \times 10^{-14}$ erg. All particles are enclosed in a square well of side $L = 112.08\sigma_1$. For convenience we shall express reduced time t^* in units of $[\epsilon/(m\sigma_1^2)]^{-1/2}$ and we shall use reduced energy and temperature units ($T^* = kT/\epsilon$, $E^* = E/\epsilon$).

The evolution of the system is followed starting from artificially created initial conditions.⁽⁸⁾ Bound states arise naturally in the course of many-body collisions. The resulting liberation of the binding energy into kinetic energy of vibrations causes increases of the kinetic temperature. This "heating up" is relatively fast and an equilibrium temperature is usually reached after $t^* \sim 500-1000$ or $t \sim 8 \times 10^{-10}-1.6 \times 10^{-9}$ sec in the laboratory time. This relaxation time depends on the total energy of the system.

A computer run of a system at $E^* = 0.7$ (equilibrium kinetic temperature $T^* = 0.802$) consisting of 100 hard-core, square-well particles was performed. In the course of this run of 42,000 full collisions in a total time $t^* = 16,808$ (laboratory time $t = 3 \times 10^{-8}$ sec) a total of 5185 dimers formed. From the data acquired in the course of this run, a histogram representing $P(N_2)$ and shown in Fig. 1 was constructed. We shall use this histogram in our assessment of the distribution of fluctuations in a closed system. The average number of dimers present in the system was $\langle N_2 \rangle = 7.032$. The average number of monomers present in the system was $\langle N_1 \rangle = 82.086$. The average number of particles that were either bound in dimers or remained monomers is equal to $\langle \tilde{N} \rangle = \langle N_1 \rangle + 2\langle N_2 \rangle = 96.15$. Let us use the approximation

$$z = \langle N_2 \rangle / \langle N_1 \rangle^2 \simeq \Omega Z_2 (\Omega Z_1)^{-2} = 1.044 \times 10^{-3} \quad (7)$$

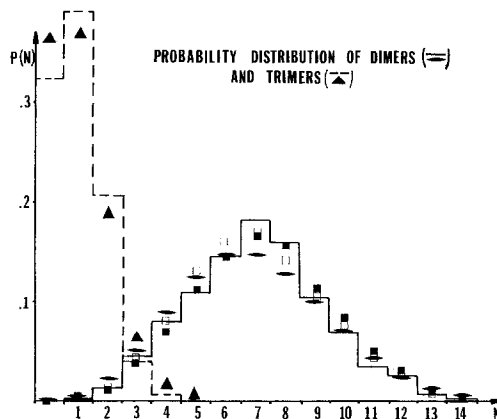


Fig. 1. The probability distribution of dimers $P(N_2)$ and trimers $P(N_3)$ for a system at equilibrium ($E^* = 0.7$). The histograms give the MD distributions, while the lens-shaped symbols and triangles show the predictions of the Poisson formula (3). The corrected formula (2) yields the results given by open squares for $\tilde{N} = 96$ and closed squares for $\tilde{N} = 100$ for the dimer distribution in a canonical ensemble.

The dependence given above is exact in a grand canonical ensemble. For a canonical ensemble, provided $\langle \tilde{N} \rangle \gg \langle N_2 \rangle$, which is the case here, it is a good approximation. With these simplifications we can write ($\Omega = 1$)

$$\{ \langle (N_2 - \langle N_2 \rangle)^2 \rangle / \langle N_2 \rangle \}_{\text{TH}} \cong [1 + 8z\tilde{N}]^{-1/2} \cong 0.745 \pm 0.05 \quad (8)$$

To calculate the variance of the dimer distribution, we can have first $\langle N_2^2 \rangle = 54.5904$, and thus

$$\{ \langle (N_2 - \langle N_2 \rangle)^2 \rangle / \langle N_2 \rangle \}_{\text{MD}} = 0.732 \pm 0.05 \quad (9)$$

in good agreement with the closed-system corrections of Van Kampen and Hanusse and in disagreement with the Poisson distribution.

Apart from statistical errors given with the estimates above, there are systematic errors that may have altered the histogram in Fig. 1. They are caused, as we have indicated before, by the existence of clusters larger than dimers, by adiabaticity, and by the finite size of the investigated system. In what follows we shall show that their influence on dimer distribution is much smaller than the dominant effects of particle number conservation.

4. INFLUENCE OF LARGER CLUSTERS AND CONSTANT ENERGY ON THE DIMER DISTRIBUTION FUNCTION

The clusters larger than dimers influence \tilde{N} , the total number of particles in monomers and dimers. We can evaluate their influence by considering a combined equilibrium distribution function, including probabilities of occurrence of configurations with larger cluster species. In effect we shall prove that the relevant range of variations of \tilde{N} is too small to alter the value of the ratio of the mean square fluctuation to the average fluctuation. A combined distribution function is given by⁽⁶⁾

$$P(N_2, N_3, \dots) = C \prod_j \frac{(\Omega Z_j)^{N_j}}{N_j!} \delta \left(\sum_j j N_j, N \right) \quad (10)$$

$\delta(i, j)$ is a Kronecker delta, and N is the total number of particles. This expression can be rewritten in an obvious fashion with the explicit use of \tilde{N} ($\tilde{N} = N - \sum_{j=3} j N_j$):

$$\begin{aligned} P(N_2; N_3, N_4, \dots) &= \{ C (\Omega Z_2)^{N_2} (\Omega Z_1)^{\tilde{N} - 2N_2} / [N_2! (\tilde{N} - 2N_2)!] \} \\ &\times \left\{ \prod_{j=3} (\Omega Z_j)^{N_j} / N_j! \right\} \delta(N_1 + 2N_2, \tilde{N}) \end{aligned} \quad (11)$$

The computer experiment histogram in Fig. 1 shows a reduced distribution function

$$P_r(N_2) = \sum_{\{N_3, N_4, \dots\}} P(N_2; N_3, N_4, \dots) \quad (12)$$

where the summation runs over all the admissible configurations of (N_3, N_4, \dots) . Such a reduced distribution function may be expressed more explicitly as

$$P_r(N_2) = \sum_{\{\tilde{N}\}} P_r(N_2; \tilde{N}) w(\tilde{N}) \quad (13)$$

where

$$P_r(N_2; \tilde{N}) = C_r (\Omega Z_2)^{N_2} (\Omega Z_1)^{\tilde{N} - 2N_2} / [N_2! (\tilde{N} - 2N_2)!]$$

and the $w(\tilde{N})$ are the probabilities that a system will contain a total of $\tilde{N} = N_1 + 2N_2$ particles available for monomer-dimer reaction:

$$w(\tilde{N}) \sim \sum_{\{N_3, N_4, \dots\}} \left[\prod_{j=3} (\Omega Z_j)^{N_j} / N_j! \right] \delta \left(\sum_{j=3} j N_j, N - \tilde{N} \right) \quad (14)$$

The weights $w(\tilde{N})$ are normalized, i.e., $\sum_{\tilde{N}} w(\tilde{N}) = 1$. In our system ($E^* = 0.7$) for the largest admissible values of \tilde{N} it follows that $w(100) + w(97) + w(96) + w(95) + w(94) = 0.97$, with the average $\langle \tilde{N} \rangle = 96.15$ and standard deviation ~ 3 . In other words, the system becomes smaller than 94 only with 3% probability. The distribution function of dimers is, in our case, insensitive to such small changes.

We may argue that errors introduced by the use of (2) with the average value of $\langle \tilde{N} \rangle$ rather than the correct, complete distribution are small [see (13)] on analytical grounds. Let us first note that an error introduced into the ratio r by $\Delta \tilde{N}$, a small variation of \tilde{N} , can be evaluated as follows:

$$\Delta[\langle (\Delta N_2)^2 \rangle / \langle N_2 \rangle] \cong 4z \Delta \tilde{N} \quad (15)$$

where $z = \Omega Z_2 / (\Omega Z_1)^2 \sim 10^{-3}$. Therefore, for typical $\Delta \tilde{N} \sim 3$ the value of the ratio is altered by $\sim 10^{-2}$, certainly less than the error indicated by the estimate (9). It may, however, happen that even if the ratio of the mean square fluctuation to the average one stays almost constant when small variations are made, $\langle N_2 \rangle$ changes by a significant amount. This could result in the increase of the ratio r in a reduced distribution, which is represented by the histogram in Fig. 1. This is certainly not the case, as we have seen from $r < 1$ obtained in a MD simulation. To have a numerical estimate of the influence of this "shifting" of N_2 , let us calculate the extremum of the distribution for $P(N_2, \tilde{N})$ and let us investigate variations of the position of this extreme with change in \tilde{N} .

It is easy to show that $P(N_2, \tilde{N})$ satisfies a recurrence relation:

$$P(N_2 + 1, \tilde{N}) = P(N_2, \tilde{N})z(\tilde{N} - 2N_2 - 1)(\tilde{N} - 2N_2 - 2) \quad (16)$$

Let us now write n , the value of N_2 for which $P(N_2)$ assumes maximum, as

$$n = z(\tilde{N} - 2n)^2 + \alpha \quad (17)$$

where $\alpha \ll n$, and $n \ll \tilde{N}$. Introducing this substitution into formula (16) for the extremum yields $\alpha \sim 3n/N^3$. Thus α is small ($\alpha \sim 10^{-5}$) and $n = z(\tilde{N} - 2n)^2$ with a good accuracy. Now it is easy to see that a small variation of \tilde{N} leads to a change in n :

$$\Delta n \simeq 2z\tilde{N} \Delta\tilde{N}$$

For typical \tilde{N} , $\Delta\tilde{N}$, and z the above equation yields $\Delta n \sim 0.6$. Therefore $\Delta N_2^2/n \sim 0.05$, at most of the order of the statistical errors indicated before. Moreover, it should be noted that this error should actually increase the value of the ratio r , making it more Poisson-like. As this change of distribution affects only the computer-experimental histogram in Fig. 1, there is little doubt that the actual molecular dynamics distribution is in fact sharper, more non-Poissonian than would be suggested by Van Kampen's corrected probability distribution. Before we ascribe this effect to the adiabaticity of the system, which will be the last point taken up in this section, let us make one further comment. The finite size of the system and resulting corrections to the average value of $\langle N_2 \rangle$ were taken into account by the coefficient α in formula (17). These corrections have proved to be of the order of $\langle N_2 \rangle / \langle \tilde{N} \rangle^3$. We expect that corrections to $\langle (N_2 - \langle N_2 \rangle)^2 \rangle$ will be of the same order for any distribution closely related to the Poisson distribution. Therefore, the finite system effects should play no detectable role for the ratio if $\alpha \ll \langle N_2 \rangle$, as it certainly is in our system.

The adiabaticity of the simulated system is the last problem we have to deal with before being able to state that the dimer distribution is definitely non-Poissonian in a manner predicted by Van Kampen. If the presence of larger clusters, considered before, tends to "wash out" the distribution, increasing the ratio, adiabaticity has an exactly opposite effect. Due to energy conservation a system containing more dimers will be hotter. This will act in a way as a negative feedback, trying to stabilize the number of dimers around some $\langle N_2 \rangle$. In fact, the discussed change of the probability distribution due to the conservation of the total number of atoms can also be treated as a negative feedback effect, where the decrease in the monomer concentration makes dimer formation less likely than dimer dissolution.

To establish which of the two feedback effects is dominant in our system, we need to evaluate the relative importance of the two conservation laws—

conservation of the total number of atoms and conservation of the total energy of the system.

Let us then estimate a typical reaction strength due to finite N . As the average value of N_2 is proportional to N , $\langle N_2 \rangle = kN$, we have for the derivative

$$d\langle N_2 \rangle / dN = k \cong 0.07$$

A typical variation of $N_2 \sim 5$ will cause a feedback effect equal to $(d\langle N_2 \rangle / dN) \times \Delta \sim 10 \times 0.07 = 0.7$.

On the other hand, the coupling constant between N_2 and the temperature with $N = 100$ can be found as the slope of the $\langle N_2(T) \rangle$ dependence.^(8,10) It is given by $d\langle N_2 \rangle / dT^* \sim 6$. The change in T^* caused by a variation of $N_2 \sim 5$ is given by $\Delta T^* = N_2 \epsilon / 2N = 0.025$. The resulting feedback effects are of the order of $(d\langle N_2 \rangle / dT^*) \times \Delta T^* \sim 0.15$. Clearly, the fact that the system conserves energy is five times "less important" than the atom number conservation requirement. With the ratio of couplings 5:1 it may nevertheless be possible that the observed narrowing of the dimer distribution beyond the value predicted by (5) is due to the adiabaticity of the system.

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