Relaxation at late stages in an entropy barrier model for glassy systems

1997 J. Phys. A: Math. Gen. 30 6671

(http://iopscience.iop.org/0305-4470/30/19/010)

J. Phys. A: Math. Gen. **30** (1997) 6671–6677. Printed in the UK PII: S0305-4470(97)84869-X

Relaxation at late stages in an entropy barrier model for glassy systems

K P N Murthy† and K W Kehr

Institut für Festkörperforschung, Forschungszentrum Jülich GmbH, D-52425 Jülich, Germany

Received 18 June 1997

Abstract. The ground-state dynamics of an entropy barrier model proposed recently for describing relaxation of glassy systems, is considered. At late stages of evolution the dynamics can be described by a simple variant of the Ehrenfest urn model. Analytical expressions for the relaxation times from arbitrary initial states to the ground state are derived. Upper and lower bounds for the relaxation times as a function of system size are obtained.

The Ehrenfest urn [1] model has played a crucial role in formulating and clarifying several fundamental and subtle concepts of statistical mechanics. In this model distinguishable balls are placed in two boxes (or urns). The dynamics consists of picking up a ball randomly and transferring it from its box to the other. Concepts like what does one mean by an equilibrium state, how does the system approach, eventually reach and thereafter persist in equilibrium, and the meaning of fluctuations that take the system away from its equilibrium state, become transparent when considering the time evolution in the Ehrenfest urn model. Interest in the Ehrenfest urn model, its variants and its generalizations has been revived recently following the work of Ritort [2]; see [3, 4] for some subsequent work on Ritort's and related models.

Ritort's model essentially describes the relaxation of a non-equilibrium system. The ground-state dynamics of Ritort's model at late stages of evolution is describable by a simple variant of the classical Ehrenfest urn model [5]. In this paper we employ first passage time formulation and obtain analytical expressions for the relaxation times from an arbitrary initial state of (the variant of) the Ehrenfest urn model.

In the model proposed by Ritort, N distinguishable balls are placed in N boxes. Energy is defined as minus the number of empty boxes. The dynamics is defined as follows. Select a ball and a box randomly and independently. If the selected box is non-empty deposit the ball in the box. If the box is empty, the transfer of the ball would increase the energy; hence carry out the transfer only with a probability given by the Boltzmann factor $\exp[-\Delta E/K_{\mathrm{B}}T]$, where ΔE $(=1)$ is the increase in the energy, K_{B} is the Boltzmann constant and T is the temperature. The static properties of this model can be calculated exactly. For example at the ground state, which is N-fold degenerate, the energy per particle is $-1+1/N$. All the balls are in one of the N boxes at the ground state. Ritort's model could explain several important characteristics of the glassy systems, like anomalously slow

† Permanent address: Theoretical Studies Section, Materials Science Division, Indira Gandhi Centre for Atomic Research, Kalpakkam 603 102, Tamilnadu, India.

relaxation, ageing, and hysteresis. Ritort's model is perhaps the first model in which only entropy barriers are present explicitly. The ground-state dynamics of the model is equivalent to an N-urn generalization and variant of the Ehrenfest model. Moving a ball to an empty box is disallowed. Thus once a box becomes empty it stays empty for ever. As a result the number of empty boxes increases with time. The energy decreases with time and eventually reaches its ground-state value. The relaxation of the energy is slow and becomes slower with time. This is easy to understand at least qualitatively, since lowering the occupancy of a box becomes less and less likely as the number of balls in the box becomes fewer and fewer. Let us denote by $\Omega(N, N)$ the set of all possible configurations of distributing N balls in N boxes. Let τ denote the time it takes for the system to relax to the ground state, averaged over the ensemble $\Omega(N, N)$ of initial configurations. It is clear that the system before reaching the ground state, arrives invariably at one of the simpler non-equilibrium configurations with only two boxes non-empty. The other $N - 2$ boxes have since been emptied during the evolution. Let us denote by $\Omega(2, N)$ the set of all possible states with N balls in 2 boxes. Also let τ_1 denote the relaxation time averaged over the ensemble $\Omega(2, N)$ of initial states. In a recent work, Lipowski [5] showed that τ_1 is less than but almost equal to τ, for large N.

The purpose of this paper can be stated as follows. Lipowski [5] derived analytical expression for the relaxation from one of the simple states belonging to the set $\Omega(2, N)$. This state consists of only one ball in one box and the remaining $N - 1$ balls in the other. Relaxation times from other states like k balls in one box and the rest in the other, were calculated through a set of recursion relations. Lipowski's work is a clever application of the formulation of Darling and Siegert [6] for first passage times of random walks. In this paper we employ a simpler and more recent first passage time formulation [7]. This method enables us to obtain closed-form expression for the relaxation time from an arbitrary initial state, a task which has not been possible in Lipowski's formulation. More importantly, employing the analytical expressions, we establish useful upper and lower bounds for the relaxation times from various initial states in terms of the system size.

We first consider the case with an even number of balls distributed in two boxes. Accordingly let $2N$ be the total number of balls in the system. Let us consider a configuration with k balls in one box and the remaining $2N - k$ balls in the other. We say the system is in state k if the number of balls in the box of lower occupancy equals k. Thus k is less than or equal to N. Let $\hat{G}_{k,k-1}(\nu)$ denote the probability that the system goes from the state k to the state $k - 1$, for the *first time* in exactly ν time steps. Thus ν is a *discrete* random variable and is called the first passage time (FPT). The first passage from k to $k - 1$ can happen in two ways: (i) Select a ball from the box containing k balls and transfer it to the other taking one time step. The probability for this is $k/2N$. At the end of this step we are in the target state $k - 1$. Hence ν, the FPT is unity. (ii) Select a ball from the box containing $2N - k$ balls and move it to the other box taking one step. The probability for this is $(2N - k)/2N$. At the end of this step we are in the state $k + 1$. Now make a first passage from the state $k + 1$ to the state $k - 1$ in the remaining $\nu - 1$ steps. The above considerations hold good for all $k \leqslant N - 1$. For $k = N$, we find that since both the boxes contain N balls each, selecting a ball from either and moving it to the other leads to the target state $k - 1$, and the FPT is unity. The state N is thus reflecting. Therefore we have

$$\begin{aligned} \hat{G}_{k,k-1}(\nu) &= \frac{k}{2N}\delta_{\nu,1} + \frac{2N-k}{2N}\hat{G}_{k+1,k-1}(\nu-1) \qquad \text{for } k = 1, 2, \ldots, N-1 \\ \hat{G}_{N,N-1}(\nu) &= \delta_{\nu,1}. \end{aligned} \tag{1}$$

The above is the complete set of N equations for the FPT densities. Since the system starting from state $k+1$ cannot reach the state $k-1$ without visiting the state k, $\hat{G}_{k+1,k-1}(\nu)$ in the above can be expressed as a convolution given by

$$\hat{G}_{k+1,k-1}(\nu) = \sum_{\eta=1}^{\nu-1} \hat{G}_{k+1,k}(\eta)\hat{G}_{k,k-1}(\nu-\eta). \tag{2}$$

The convolution in the above holds good in general for one-dimensional problems with nearest-neighbour hopping.

When the number of balls is odd, say $2N-1$, the equations for the FPT densities remain formally the same except that the state $N-1$ is now *reflecting*, in the following sense. Consider the first passage from the state $N-1$ to the state $N-2$, in ν steps. There are two ways: (i) Move a ball from the box containing $N-1$ balls to the other box, in one step; the probability for this is $(N-1)/(2N-1)$. At the end of this step we are in the target state $N-2$. Hence the FPT is unity. (ii) Move a ball from the box containing N balls to the other box, taking one time step. The probability for this is $N/(2N-1)$. At the end of this step we are in state $N-1$, the same state we started with. Now make a first passage from this state $N-1$ to the target state $N-2$ in the remaining $\nu-1$ steps. Thus for an odd number of balls we get

$$\begin{aligned}
\hat{G}_{k,k-1}(\nu) &= \frac{k}{2N-1}\delta_{\nu,1} + \frac{2N-1-k}{2N-1}\hat{G}_{k+1,k-1}(\nu-1) \qquad \text{for } k = 1, 2, \ldots, N-2 \\
\hat{G}_{N-1,N-2}(\nu) &= \frac{N-1}{2N-1}\delta_{\nu,1} + \frac{N}{2N-1}\hat{G}_{N-1,N-2}(\nu-1).
\end{aligned} \tag{3}$$

The above constitute the complete set of $N-1$ equations for the FPT densities for the case with an odd number of balls. To solve the recursion relations (1) and (3) for the first passage time densities we employ generating function technique.

Let $G_{i,j}(Z)$ denote the generating function for the FPT, defined as

$$G_{i,j}(Z) = \sum_{\nu=1}^{\infty} Z^{\nu}\hat{G}_{i,j}(\nu). \tag{4}$$

Multiplying both sides of (1) by Z^{ν} and summing over ν from 1 to ∞, we get

$$\begin{aligned}
G_{k,k-1}(Z) &= Z\frac{k}{2N} + Z\frac{2N-k}{2N}G_{k+1,k-1}(Z) \qquad \text{for } k = 1, \ldots, N-1 \\
G_{N,N-1}(Z) &= Z.
\end{aligned} \tag{5}$$

Equivalent relations, not given here, can be obtained for the case with an odd number of balls. From equations (5), a terminating continued fraction relation for $G_{k,k-1}(Z)$ can be derived by noting that $G_{k+1,k-1}(Z) = G_{k+1,k}(Z) \times G_{k,k-1}(Z)$, by virtue of the convolution theorem. Substituting the convolution in (5), we get

$$\begin{aligned}
G_{k,k-1}(Z) &= \frac{Z\frac{k}{2N}}{1 - Z\frac{2N-k}{2N}G_{k+1,k}(Z)} \qquad \text{for } k = 1, \ldots, N-1 \\
G_{N,N-1}(Z) &= Z.
\end{aligned} \tag{6}$$

In fact, by convolution we have $G_{m,0}(Z) = \prod_{k=1}^{m} G_{k,k-1}(Z)$, for $m = 1, \ldots, N$. Thus in principle we have obtained the distribution of relaxation time from an arbitrary state belonging to $\Omega(2, N)$, to the zero ground state, though the expressions are in Z space.

To calculate the mean first passage time (MFPT), from the state k to the state $k-1$, we differentiate $G_{k,k-1}(Z)$ with respect to Z and set $Z=1$. Let $F_{k,k-1}$ denote the MFPT from k to $k-1$. For the problem with an even number of balls, we get

$$\begin{aligned} F_{k,k-1} &= \frac{2N-k}{k} F_{k+1,k} + \frac{2N}{k} \qquad \text{for } k=1,\ldots,N-1 \\ F_{N,N-1} &= \left(\frac{1}{2}\right)\ \frac{2N}{N}. \end{aligned} \tag{7}$$

The above can be cast in a convenient matrix notation

$$|F\rangle = A|F\rangle + |U\rangle \tag{8}$$

where $|F\rangle$ is a column vector $(F_{1,0} \quad F_{2,1} \quad \cdots \quad F_{N,N-1})^{\dagger}$ and $|U\rangle$ is the column vector representing the inhomogeneities, $(2N/1 \quad 2N/2 \quad \cdots \quad 1)^{\dagger}$. Here the superscript † denotes the transpose operation. The $N \times N$ matrix A has elements given by $A_{i,j} = \delta_{i,j-1} \times (2N-i)/i$. We can cast (8) as $B|F\rangle = |U\rangle$ where $B = I - A$. The matrix B has all its diagonal elements unity; all the other elements except those in the first upper diagonal are zero. The matrix elements of B are given by

$$B_{i,j} = -\left(\frac{2N-i}{i}\right) \times \delta_{i,j-1} + \delta_{i,j}. \tag{9}$$

Below we give the matrix B explicitly, to enable easy visualization of the solutions we will derive shortly.

$$B = \begin{pmatrix} 1 & -\left(\frac{2N-1}{1}\right) & 0 & 0 & 0 & \cdot \\ 0 & 1 & -\left(\frac{2N-2}{2}\right) & 0 & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ 0 & 0 & 0 & 0 & 1 & -\left(\frac{2N-(N-1)}{2N}\right) \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix}. \tag{10}$$

To calculate the mth element $F_{m,m-1}$ of the vector $|F\rangle$, we replace the mth column of the matrix B by the vector $|U\rangle$. Let the matrix thus formed be denoted by $B_{(m)}$. Then $F_{m,m-1}$ is given by Cramer's rule

$$F_{m,m-1} = \frac{D[B_{(m)}]}{D[B]} \tag{11}$$

where $D[\cdot]$ denotes the determinant. First we observe that the determinant of the matrix B is unity. The problem reduces to calculating the determinant of $B_{(m)}$.

Let us consider the case with $m=1$. The determinant of $B_{(1)}$ can be easily written down by inspection as

$$\begin{aligned} F_{1,0} = D\left[B_{(1)}\right] = \frac{2N}{1} + \frac{2N}{2}\left(\frac{2N-1}{1}\right) + \frac{2N}{3}\left(\frac{2N-1}{1}\right)\left(\frac{2N-2}{2}\right) \\ + \cdots \\ + \frac{1}{2} \quad \frac{2N}{N}\left(\frac{2N-1}{1}\right)\left(\frac{2N-2}{2}\right)\cdots\left(\frac{2N-(N-1)}{N-1}\right) \end{aligned} \tag{12}$$

which can be cast in a compact form as sum over products given by

$$F_{1,0} = \sum_{n=1}^{N} \frac{2N}{n} \left(1 - \frac{1}{2}\delta_{n,N}\right) \prod_{k=1}^{n-1} \frac{2N-k}{k}.$$

$$= \sum_{n=1}^{N-1} {}^{2N}C_n + \left(\frac{1}{2}\right) {}^{2N}C_N \tag{13}$$

where ${}^{(\cdot)}C_{(\cdot)}$ are the usual binomial coefficients. Noting that ${}^{2N}C_n$ is the same as ${}^{2N}C_{2N-n}$, we see immediately that

$$2 \times F_{1,0} = \sum_{n=1}^{2N-1} {}^{2N}C_n. \tag{14}$$

Add the binomial coefficients ${}^{2N}C_0 = 1$ and ${}^{2N}C_{2N} = 1$ to both sides of the equation above. We find that the right-hand side becomes 2^{2N}, and we get

$$F_{1,0} = 2^{2N-1} - 1 \tag{15}$$

which is precisely the expression derived by Lipowski [5]. Note that in Lipowski's paper N denotes the total number of balls, whereas here the total number of balls is taken as even ($2N$), see equation (15), or odd ($2N-1$), see equation (22). We have considered the two cases separately to bring out clearly the subtle difference in the reflecting boundary while deriving the master equations, see equations (1) and equations (3).

Let us now derive closed-form expressions for $F_{m,m-1}$. To this end, we replace the mth column of the matrix B by the vector $|U\rangle$ and construct the matrix $B_{(m)}$, whose determinant gives

$$F_{m,m-1} = \sum_{n=m}^{N-1} \left(\frac{2N}{n}\right) \prod_{k=m}^{n-1} \frac{2N-k}{k} + \left(\frac{1}{2}\right)\left(\frac{2N}{N}\right) \prod_{k=m}^{N-1} \frac{2N-k}{k}. \tag{16}$$

First we multiply both sides of the above equation by $\prod_{k=1}^{m-1}(2N-k)/k \equiv (m/2N)\ {}^{2N}C_m$, and get,

$$\left(\frac{m}{2N}\right) {}^{2N}C_m\ F_{m,m-1} = \sum_{n=m}^{N-1} \left(\frac{2N}{n}\right) \prod_{k=1}^{n-1} \frac{2N-k}{k} + \left(\frac{1}{2}\right)\left(\frac{2N}{N}\right) \prod_{k=1}^{N-1} \frac{2N-k}{k}$$

$$= \sum_{n=m}^{N-1} {}^{2N}C_n + \left(\frac{1}{2}\right) {}^{2N}C_N. \tag{17}$$

Now add to both sides of the above equation the term $\sum_{n=1}^{m-1} {}^{2N}C_n$, and get

$$\sum_{n=1}^{m-1} {}^{2N}C_n + \left(\frac{m}{2N}\right) {}^{2N}C_m F_{m,m-1} = \sum_{n=1}^{N-1} {}^{2N}C_n + \left(\frac{1}{2}\right) {}^{2N}C_N. \tag{18}$$

We see immediately that

$$2 \times \left[\sum_{n=1}^{m-1} {}^{2N}C_n + \left(\frac{m}{2N}\right) {}^{2N}C_m F_{m,m-1}\right] = \sum_{n=1}^{2N-1} {}^{2N}C_n. \tag{19}$$

If we now add ${}^{2N}C_0 = 1$ and ${}^{2N}C_{2N} = 1$ to both sides of the above equation, we find the right-hand side is simply 2^{2N}. We get

$$F_{m,m-1} = \left(\frac{2N}{m}\right)\left(\frac{1}{{}^{2N}C_m}\right)\left[\left(2^{2N-1} - 1\right) - \sum_{n=1}^{m-1} {}^{2N}C_n\right]. \tag{20}$$

It can easily be seen that if we substitute $m = 1$ in the above we recover Lipowski's result [5], also derived explicitly in this paper, see equation (15). The relaxation time from any state k to the zero ground state can be obtained by summing equation (20) over m from 1 to k. Thus we get

$$F_{k,0} = \sum_{m=1}^{k} \left(\frac{2N}{m}\right) \left(\frac{1}{{}^{2N}C_m}\right) \left[\left(2^{2N-1} - 1\right) - \sum_{n=1}^{m-1} {}^{2N}C_n \right]. \tag{21}$$

For an odd number of balls the derivation proceeds in the same way, and we get

$$F_{k,0} = \sum_{m=1}^{k} \left(\frac{2N-1}{m}\right) \left(\frac{1}{{}^{2N-1}C_m}\right) \left[\left(2^{2N-2} - 1\right) - \sum_{n=1}^{m-1} {}^{2N-1}C_n \right]. \tag{22}$$

Now that we have an analytical expression for the relaxation time, $F_{k,0}$, from an arbitrary state, we can estimate how much it deviates from $F_{1,0}$ when the system size goes to infinity. From equation (20) it is clear that

$$F_{1,0} > F_{2,1} > F_{3,2} > \cdots > F_{N-1,N-2} > F_{N,N-1} \; (= 1). \tag{23}$$

In fact for large N, from equation (20) we have

$$F_{m,m-1} \underset{N\to\infty}{\sim} F_{m-1,m-2} \left(\frac{m-1}{2N}\right) \tag{24}$$

which implies that

$$F_{m,m-1} \underset{N\to\infty}{\sim} F_{1,0} \; \frac{(m-1)!}{(2N)^{m-1}}. \tag{25}$$

Since, $F_{k,0} = F_{1,0} + F_{2,1} + \cdots + F_{k,k-1}$, we have

$$F_{k,0} \underset{N\to\infty}{\sim} F_{1,0} \left[1 + \frac{1}{2N} + \frac{2}{(2N)^2} + \frac{6}{(2N)^3} + \cdots + \frac{(k-1)!}{(2N)^{k-1}} \right] \tag{26}$$

for all k. Thus to order N^{-1}, we have

$$F_{k,0} \underset{N\to\infty}{\sim} F_{1,0} \left(1 + \frac{1}{2N}\right) \tag{27}$$

for all $k \geqslant 2$ and the correction is independent of k. In fact it can easily be shown from equation (26) that

$$F_{1,0} \left(1 + \frac{1}{2N}\right) < F_{k,0} < F_{1,0} \left(1 + \frac{1}{N}\right) \tag{28}$$

for all $k \geqslant 2$, when N is large. Thus it is clear that, indeed $F_{1,0}$ is the principal time scale in the problem and relaxation time from any other state is only negligibly greater than $F_{1,0}$ for large systems.

This paper in a way complements the work of Lipowski [5]. We have obtained analytical expressions for the relaxation times to the ground state (with all the balls in one box and the other box empty), starting from an arbitrary initial state (with, say, k balls in one box and the rest in the other). We have shown that the relaxation time from the simple state $k = 1$ (with one ball in one box and the rest in the other) sets the principal time scale in the problem; relaxation from other states takes negligibly more time than this, for large systems. A natural question that arises in this context is whether we can construct a simple two-urn analogue of Ritort's model. To this end we need to suitably modify the energy function defined over the states of $\Omega(2, N)$. For example, we can define energy as minus the absoluted value of the difference of the number of balls in the two boxes, i.e. $E(n) = 2n - N$, where $n \leqslant N/2$ is the number of balls in the lower occupancy box (defining the state of the system) and N is the total number of balls. It is easily seen that the state $n = 0$ is the minimum energy ground state with $E(0) = -N$. The maximum energy state is $n = N/2$, with $E(N/2) = 0$. It can be shown that an arbitray state k relaxes to the ground state in a time given by $N \sum_{m=1}^{k} m^{-1}$, at zero temperature. However, as the temperature increases, the relaxation of energy to its equilibrium value (at that temperature) becomes faster. It is indeed worthwhile investigating if other features like hysteresis and ageing are also present in this simple model.

Acknowledgment

KPNM thanks Forschungszentrum Jülich, for the hospitality extended to him at the Institut für Festkörperforschung.

References

[1] Ehrenfest P 1912 *The Conceptual Foundations of the Statistical Approach in Mechanics* transl. M J Moravcsik 1959 (Ithaca, NY: Cornell University Press)
See also:
Klein M J (ed) 1959 *Paul Ehrenfest, Collected Scientific Papers* (Amsterdam: North-Holland)
[2] Ritort F 1995 *Phys. Rev. Lett.* **75** 1190
[3] Godreche C, Bouchaud J P and Mezard M 1995 *J. Phys. A: Math. Gen.* **28** L603
[4] Godreche C and Luck J M 1996 *J. Phys. A: Math. Gen.* **29** 1915
[5] Lipowski A 1997 *J. Phys. A: Math. Gen.* **30** L91
[6] Darling D A and Siegert A F J 1953 *Ann. Math. Stat.* **24** 624
[7] Murthy K P N and Kehr K W 1989 *Phys. Rev* A **40** 2082
See also:
Zwerger W and Kehr K W 1980 *Z. Phys.* B **40** 157