Evaluation of the energy barrier distribution in many-particle systems using the path integral approach

LETTER TO THE EDITOR

Evaluation of the energy barrier distribution in many-particle systems using the path integral approach

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Abstract. We present a numerical method for the evaluation of the distribution of energy barriers between metastable states in many-particle systems with arbitrary interparticle interaction. The method is based on the search for the optimal path between the two given metastable states using the minimization of the corresponding action occurring in the Onsager–Machlup functional for the probability of transition between these two states.

The problem of evaluating the probability of transition between metastable states in various systems with many degrees of freedom is one of the most important and difficult tasks in many areas of physics [1], particularly in studying disordered systems (like spin glasses) with a strong interparticle interaction where disorder and frustration make both analytical and numerical calculations extremely difficult (see the review articles [2, 3]).

For energy barriers ΔE comparable with the temperature T, direct Monte Carlo simulations of the escape over the barrier based on the Langevin equations are possible [1, 4, 5]. However, for the most interesting situation—high energy barriers (or in the low-temperature limit $T \ll \Delta E$)—such simulations are almost useless because the mean escape time grows exponentially with the barrier height. On the other hand, in this case the task is somewhat simpler because it is sufficient to find the lowest saddle point (its height will give the corresponding energy barrier ΔE) between the two chosen energy minima and then calculate the transition probability p using the Arrhenius–Van't Hoff formula ($p \sim \exp(-\Delta E/T)$).

Unfortunately reliable analytical and semi-analytical methods for searching for saddle points in such systems are applicable only for the single-particle case [6, 7] and the few-particle case (for one of the latest attempts, see [8]), so the problem is still far from its final solution. In this letter we propose a method for energy barrier evaluation based on the search for the optimal transition path between the two given metastable states by minimizing the corresponding action derived from the path integral formulation of the problem.

To explain the basic idea, we start with a system of N classical particles having coordinates $\boldsymbol{x} = (x_1, \ldots, x_N)$ and velocities $\dot{\boldsymbol{x}}$. The equations of motion for these particles in the presence of thermal fluctuations (Langevin equations) can be written as

$$\dot{x}_i = -\frac{\partial V(\boldsymbol{x})}{\partial x_i} + \xi_i(t) \qquad i = 1, \ldots, N \tag{1}$$

where $V(\boldsymbol{x})$ is the system energy including the interparticle interactions; we have neglected the inertial term for the sake of simplicity and absorbed the friction constant into the time scaling. Random (thermal) Langevin forces ξ_i can be considered in most cases as

independent Gaussian random quantities with zero correlation time [1]: $\langle \xi_i(0)\xi_j(t)\rangle = 2D\delta_{ij}\delta(t)$ (where $D \sim T$). Using these assumptions and rewriting the equations (1) as $\xi_i(t) = \dot{x}_i + \partial V(\boldsymbol{x})/\partial x_i$, we immediately obtain that the probability of observing a given trajectory $\boldsymbol{x}(t)$ for the transition between the two states A and B during the time t_f ($\boldsymbol{x}_A(0) \to \boldsymbol{x}_B(t_f)$) is [9, 10]

$$P[\boldsymbol{x}(t)] \simeq J[\boldsymbol{x}]\exp\left[-\frac{S(\boldsymbol{x}(t))}{4D}\right] \tag{2}$$

where $J[\boldsymbol{x}(t)]$ is the Jacobian of the variable transformation $\boldsymbol{x} \to \boldsymbol{\xi}$ and the *action* $S(\boldsymbol{x}(t))$ is defined as

$$S(\boldsymbol{x}(t), t_f) = \int_0^{t_f} \mathrm{d}t \, \sum_i \left(\frac{\mathrm{d}x_i}{\mathrm{d}t} + \frac{\partial V(\boldsymbol{x})}{\partial x_i}\right)^2. \tag{3}$$

The total transition probability $P_{\mathrm{tot}}(A \to B, t_f)$ is then given by the integral of (2) over all paths $\boldsymbol{x}(t)$. Evaluation of this path integral is an immense task for any strongly interacting system. However, in the low-temperature limit it is evident that the main contribution to P_{tot} comes from the trajectories which are close to the optimal trajectory $\boldsymbol{x}_{\mathrm{opt}}(t)$, i.e. to the trajectory which minimizes the action $S(\boldsymbol{x}(t))$, and the energy barrier for the given transition can be found as the barrier along this trajectory: $\Delta E(A \to B) = E_{\mathrm{max}}(\boldsymbol{x}_{\mathrm{opt}}) - E_A$. The problem that we are left with is the minimization of the functional $S(\boldsymbol{x})$.

It is obviously impossible to minimize it analytically for any realistic model. Among the two main numerical possibilities—(i) solution of the boundary value problem for the Euler–Lagrange equation(s) for this functional and (ii) minimization of the many-variable function resulting from the approximation of the integral (3) by some numerical quadrature formula—we have chosen the latter method as the faster one. Dividing the time interval $[0, t_f]$ into K slices and approximating (3) by the simplest quadrature, we obtain

$$S_{\mathrm{disc}}(\boldsymbol{x}) = \Delta t \sum_{k=0}^{K-1} \sum_{i=1}^{N} \left[\frac{x_{i,k+1} - x_{i,k}}{\Delta t} + \frac{1}{2}\left(\frac{\partial V\{\boldsymbol{x}_{k+1}\}}{\partial x_{i,k+1}} + \frac{\partial V\{\boldsymbol{x}_k\}}{\partial x_{i,k}}\right)\right]^2 \tag{4}$$

where $\Delta t = t_f/K$, $x_{i,k}$ is the coordinate of the ith particle at the time $t_k = k\,\Delta t$ and $\boldsymbol{x}_k$ denotes the set of all particle coordinates for the kth slice.

For the determination of the number of slices K necessary for the accurate determination of the energy barrier we have minimized the action (4) with the constant time step Δt and various Ks. Starting from some small K ($K_1 = 16$) we increased it for the next action minimization ($K_{l+1} = 2K_l$) until the relative difference between the energy barriers obtained for the subsequent minimizations was sufficiently small (less than 1%: $|(E_l - E_{l+1})/E_l| < 0.01$).

As the simplest possible test of the whole method, we have calculated an optimal trajectory for a particle moving in the 2D space (x_1, x_2) between the two minima in the potential

$$V(\boldsymbol{x}) = \sum_j \frac{U_j}{1 + ((\boldsymbol{x} - \boldsymbol{r}_j)/\Delta_j)^2} \tag{5}$$

where the parameter $\boldsymbol{r}_j$ determines the position and Δ_j the width of the jth peak ($U_j > 0$) or hole ($U_j < 0$). The result of such a test for the energy surface possessing two peaks P_1 and P_2 and two holes M_1 and M_2 is shown in figure 1. The starting trajectory for the minimization process was a straight line between M_1 and M_2. The final trajectory shown in figure 1 clearly passes through a saddle point providing the correct value of the energy barrier.

For many-particle systems of real interest with the particle number $N \gg 1$, the discrete action (4) depends on a huge number of variables ($\sim NK$) which makes its minimization very time consuming. But although technically very difficult, the minimization of (4) is not itself the main problem in the optimal trajectory search. The main problem is the presence of many 'false' local minima of the functional (3), i.e. trajectories between the two states which minimize (3) but do not provide any information about the corresponding energy barriers.
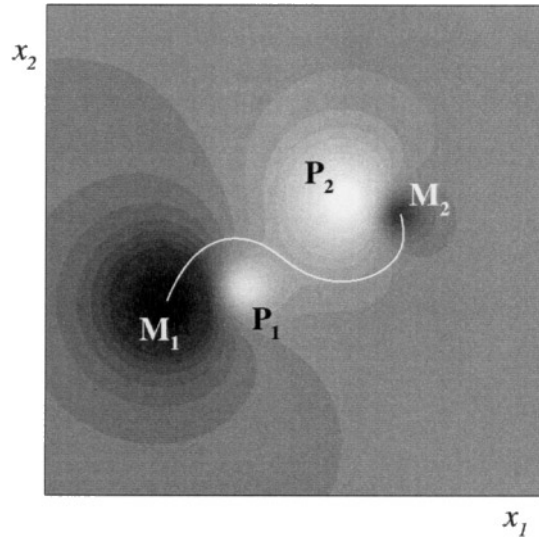
Figure 1. The optimal trajectory (white line) for the particle transition between the two minima M_1 and M_2 for the potential of the type (5) found by the minimization of the action (4). The grey-scale map is used to show the potential values.

Such a variety of the local minima of the action is due to the following two facts [11]. First, any trajectory (path) which goes between the two energy minima along the gradient lines of the energy surface (i.e. for which $\dot{x}_i = \pm \partial V\{x\}/\partial x_i$) provides a local extremum to the action $S(x)$. Second, the $S(x)$-value along the optimal path depends only on the sum of the energy barriers ΔE which the path has to climb over.

Using the first statement it is easy to construct an example of an energy surface where there would exist two optimal trajectories between the given energy minima where (i) the first trajectory goes through some intermediate energy minimum, thus climbing subsequently over two energy barriers, and (ii) the second path goes through the energy maximum (but still along the gradient lines). If, in addition, the sum of the two barriers along the first path is equal to the height of the energy maximum on the second trajectory, the action values for the two trajectories would be the same. Thus no algorithm based on action evaluation alone would be able to choose between these two paths, which are from our point of view clearly *not* equivalent, because the second trajectory does not contain any information about the energy barriers in the system.

For this reason we have constructed a special algorithm which is able to distinguish between the two kinds of optimal trajectory described above by analysing the trajectories themselves. The algorithm (details of which will be published elsewhere) checks whether the trajectory goes through a saddle point or an energy maximum by minimizing the energy starting from the points lying in the vicinity of the optimal trajectory and analysing local minima on the energy landscape obtained this way. In all of our tests the algorithm could extract 'true' optimal trajectories from a large variety of the paths found by action minimization with different starting trajectories.

To demonstrate the implementation of the method for the systems of interacting magnetic moments we consider for definiteness a system of small identical absolutely single-domain ferromagnetic particles with the volume V and the saturation magnetization M_s; the extension of the method to a classical spin glass of any kind is obvious. It is convenient to start with the system of the Landau–Lifshitz–Gilbert equations of motion for the reduced particle magnetizations $m_i = M_i/M_s$ in the presence of thermal fluctuations (see [12] for details):

$$\frac{\mathrm{d}m_i}{\mathrm{d}t} = \gamma \left[m_i \times \left(h_i^{\mathrm{eff}} - \eta \frac{\mathrm{d}m_i}{\mathrm{d}t} + h_i^L \right) \right] \qquad i = 1, \ldots, N \qquad (6)$$

where $\gamma = M_s \gamma_0$ (γ_0 is the gyromagnetic ratio), η denotes the dissipation constant and the reduced fields $h = H/M_s$ have been introduced. The random (Langevin) field h_i^L simulates the effect of thermal fluctuations and the 'usual' effective field h_i^{eff} is the negative derivative of the system energy E (measured in units of $M_s^2 V$) over the corresponding magnetization: $h_i^{\mathrm{eff}} = -\partial E/\partial m_i$. In the large-dissipation limit $\eta\gamma \gg 1$ (which means the same as neglecting the inertial term in (1)) this equation can be rewritten in the form

$$\dot{m}_i = -\left[m_i \times [m_i \times h_i^{\mathrm{tot}}] \right] = -m_i(m_i \cdot h_i^{\mathrm{tot}}) + h_i^{\mathrm{tot}} \qquad (7)$$

where all of the constants are absorbed in the time unit, the total field is $h^{\mathrm{tot}} = h^{\mathrm{eff}} + h^L$ and the normalization $m_i^2 = 1$ was used in the last transformation.

Changing to the spherical coordinate system (SCS) for the magnetic moments (so that, as usual, $m_i^x = \sin\theta_i \cos\phi_i$, $m_i^y = \sin\theta_i \sin\phi_i$, $m_i^z = \cos\theta_i$) we obtain the required equations of motion for the magnetization angles:

$$\dot{\theta}_i = -\frac{\partial E\{\Omega\}}{\partial \theta_i} + h_{i,x'}^L \qquad (8)$$

$$\sin\theta_i \dot{\phi}_i = -\frac{1}{\sin\theta_i} \frac{\partial E\{\Omega\}}{\partial \phi_i} + h_{i,y'}^L \qquad (9)$$

where $h_{i,x'}^L$ and $h_{i,y'}^L$ are Cartesian components of the Langevin field in the coordinate systems 'attached' to the ith magnetic moment. The components of h^{eff} are already expressed as the corresponding angular derivatives of the system energy $E\{\Omega\}$ (where Ω denotes the set of all of the angles (θ_i, ϕ_i)) which may include interparticle interaction of any kind, i.e. exchange, RKKY or dipolar.

The system (9) is fully analogous to (1), so under the same assumptions concerning the Langevin field, the action for the transition path $\Omega(t)$ between the two chosen magnetization states Ω_A and Ω_B is

$$S[\Omega(t)] = \int_0^{t_f} \mathrm{d}t \sum_i \left[\left(\frac{\mathrm{d}\theta_i}{\mathrm{d}t} + \frac{\partial E\{\Omega\}}{\partial \theta_i} \right)^2 + \left(\sin\theta_i \frac{\mathrm{d}\phi_i}{\mathrm{d}t} + \frac{1}{\sin\theta_i} \frac{\partial E\{\Omega\}}{\partial \phi_i} \right)^2 \right]. \qquad (10)$$

The magnetization path in the Ω-space which minimizes this functional can provide information about the energy barrier separating the states Ω_A and Ω_B in the same way as for a system of 'usual' particles (see above).

To find this optimal path, we have minimized the discrete representation of the action (10) (analogous to (4)) as a function of the orientation angles $(\theta_{i,k}, \phi_{i,k})$. The checking procedure mentioned above was applied to each path found in this way to ensure that it really passes through the saddle points. The energy barrier encountered along the 'true' optimal trajectory was assumed to be the lowest barrier between the states Ω_A and Ω_B.

The minimization procedure for the discrete representation of (10) is subject to the stability problems specific to the spherical coordinates: the factors $1/\sin\theta_i$ in (10) diverge

for any trajectory closely approaching the polar axis of the corresponding SCS ($\theta_i \to 0$ or $\theta_i \to \pi$). For this reason one has to choose a suitable SCS for each particle separately at the beginning of the minimization procedure and also to switch to another set of spherical coordinates for particles whose trajectories become too close to the polar axis of their SCS during the minimization process. This prevents, in particular, the use of the most powerful standard minimization technique—the conjugate gradient method [13]. For this reason we have chosen for the action minimization the improved version of the 'equation-of-motion' method (see, e.g., reference [13]). This improved version was developed by A Hubert, K Ramstöck and the author and is described in [14].

The method was first tested on a single particle having uniaxial magnetic anisotropy with the energy $E_{an} = 0.5\beta M_s^2 V \sin^2 \psi$, where β is the reduced anisotropy constant (for the easy-axis case, $\beta > 0$) and ψ is the angle between the easy axis n and the particle moment m. In the absence of the external field such a particle has two equivalent (meta)stable magnetization states along the two opposite directions of the anisotropy axis separated by the reduced energy barrier $\epsilon \equiv E/(M_s^2 V) = \beta/2$. The barrier found by our algorithm agreed with this value within the numerical accuracy.
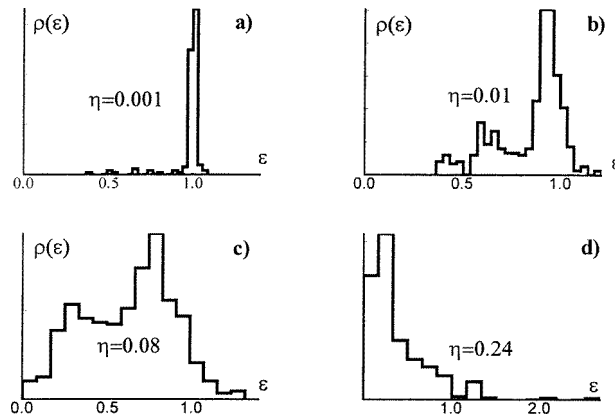
Figure 2. Energy barrier distributions found by our algorithm for the system of $N = 128$ 'dipolarly' interacting magnetic particles with the uniaxial anisotropy ($\beta = 2.0$) for various particle volume fractions η as shown in the figure.

In the next test a system of $N = 128$ *non-interacting* particles with different anisotropy constants β_i was considered, which has (in the absence of the external field) 2^N energy minima with the same (zero) energy. From the physical point of view it is evident that transitions between these local minima occur via the single-particle moment jumps between the opposite directions of the anisotropy axis. In all of the cases studied, our algorithm was indeed able to find the connected path between the two chosen energy minima consisting of the single-moment flops (i.e. the transition trajectory which passed through the saddle points only). The energy barriers along this path for the jump of the ith moment agreed with the values evaluated as $\epsilon_i = \beta_i/2$.

The last test was performed for a system of $N = 128$ *'dipolarly' interacting* particles with equal anisotropies $\beta_0 = 2.0$. The particles were positioned randomly but not overlapping in the cubic volume; periodic boundary conditions were assumed.

The energy barrier distribution for various particle volume concentrations η obtained by our algorithm is shown in figure 2. The following numbers of transitions between various pairs of the metastable system states which passed through the saddle points were

found and used to build the histograms in figure 2: for $\eta = 0.001$, $N_{tr} = 90$ transitions; for $\eta = 0.01$, $N_{tr} = 194$ transitions; for $\eta = 0.08$, $N_{tr} = 266$ transitions; and for $\eta = 0.24$, $N_{tr} = 159$ transitions (the number of energy barriers was correspondingly twice as large). The whole calculation took about two weeks on the HP-Workstation 712/60 (60 MHz, 32 Mbyte RAM, program code written in Fortran).

As expected, for the lowest concentration ($\eta = 0.001$; figure 2(a)), where the interactions are negligible, almost all of the barriers are nearly equal to the single-particle barrier $\epsilon = \beta_0/2 = 1.0$. For the next volume concentration $\eta = 0.01$ (figure 2(b)), there already exist a considerable number of barriers with other (mostly lower) values. They arise due to the quite strong interaction of closely positioned (by chance) particles: the reduced interaction field from the nearest possible neighbour h_{max}^{dip} $(=H_{max}^{dip}/M_s) \sim 1$ is of the same order of magnitude as the maximal anisotropy field $h_{max}^{an} \sim \beta_0 = 2.0$. For systems with moderate ($\eta = 0.08$; figure 2(c)) and high ($\eta = 0.24$; figure 2(d)) concentrations the energy barrier distribution is qualitatively different: it is shifted towards the lower energies, so for $\eta = 0.24$ the low-energy barriers clearly dominate.

Although our results for interacting systems are preliminary, some comments concerning their possible comparison with the experiment are in order (unfortunately there are to our knowledge no analogous theoretical results). There are at least two kinds of measurement which our results can be related to:

(i) measurements of the magnetic viscosity in fine-particle systems indicate faster relaxation for higher particle concentrations η (see, e.g., [15, 16]), thus seeming to support our conclusion that the barrier distribution is shifted towards the lower energies when η increases; and

(ii) studies of the concentration dependence of the ac susceptibility for the frozen ferrofluids (like those presented in [17]) show that the interparticle interactions lead to higher energy barriers, which contradicts our results.

Here we would just like to point out that the establishing of the relationship between all of these experiments and our data is by no means trivial, for at least the following reasons (apart from the obvious one that real systems always have a broad distribution of single-particle parameters):

(i) all of the experiments were performed at finite (and not even at *low*) temperatures, so the density of *free*-energy barriers is required for their interpretation;

(ii) different moment changes occur by transitions over different barriers; and

(iii) due to the interparticle interaction each transition changes the heights of other barriers.

Clearly further investigations are necessary.

In conclusion, we have developed and tested a numerical method suitable for the calculation of the energy barrier distribution in many-particle systems with continuous degrees of freedom and arbitrary interparticle interaction.

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