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Umbrella sampling in non-equilibrium computer simulations

Ronald Blaak [1], Hartmut Löwen [*]

Institut für Theoretische Physik II, Heinrich-Heine-Universität, Universitätsstraße 1, D-40225 Düsseldorf, Germany

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Abstract

We describe the application of the umbrella sampling technique well known from equilibrium Monte Carlo to dynamical, non-equilibrium simulations. This method is used specifically to calculate the nucleation barrier of Brownian Yukawa particles in a homogeneous shear flow.

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1. Introduction

Umbrella sampling is an often used tool in equilibrium simulations to obtain information of processes or events that require extremely long simulation times to be observed. An example of such a process is nucleation of a stable phase in an unstable bulk phase. Due to fluctuations in a super-cooled liquid, for example, one can observe the continuous formation and annihilation of small crystalline structures. Even though such a super-cooled system is only meta-stable, the system will in general not crystallize immediately. According to classical nucleation theory [1,2], there are two counteracting contributions at work. On the one hand the system gains free energy by forming a small crystalline cluster, because the free energy per particle for the crystal is lower than that of the surrounding liquid. On the other hand, the formation of a nucleus will also require the creation of an interface between the crystalline nucleus and the liquid, which will cost free energy. The result of these two counteracting contributions is that it is unfavorable for small nuclei to grow bigger, but once a nucleus is large enough, the critical nucleus size, the other effect takes over and the nucleus will prefer to grow larger.

In terms of statistical physics this means that a nucleus will have a very low probability to be found, in other words has a very low Boltzmann weight. Therefore one would need in general very long simulation times in order to observe a nucleation event. That it is nevertheless possible to simulate such rare events

* Corresponding author.
E-mail address: hlowen@thphy.uni-duesseldorf.de (H. Löwen).
[1] Current address: Department of Chemistry, Cambridge University, Lensfield Road, Cambridge, CB2 1EW, United Kingdom.

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and obtain sufficient statistics is due to the umbrella sampling technique in Monte Carlo simulations. It has been introduced by Torrie and Valleau [3] and is based on the sampling of a modified Hamiltonian. Rather than performing the system with its natural interaction, an additional potential is added to the Hamiltonian. This biasing potential is chosen in such a way that it restricts the system to the part of phase space of interest. In the case of nucleation [4], one can for instance use a harmonic-shaped potential depending on the difference of the size of the nucleus with some preferred size. For this biased Hamiltonian, the minimum energy state will be one where the size of the nucleus is that of the preferred size that has been chosen. The harmonic part that has been added will now prevent that the cluster shrinks too much or grows too large. By performing simulations for different parameters of the bias, i.e. the preferred cluster size, one can now obtain information on clusters of any size, even though those clusters might never appear in an unbiased simulation.

Umbrella sampling, however, as it stands is an *equilibrium technique*. As such one would expect that it cannot be used in non-equilibrium situations. Here we will explain why and how it can work in a dynamical simulation. More specifically, the way it is applied in the case of simulating crystal nucleation under shear [5,6]. Although we explain the method in detail and specifically for the use in crystal nucleation, it can be easily be applied to other situations. We describe such situations in the last chapter.

2. Umbrella sampling in non-equilibrium

In order to obtain information on rare, non-equilibrium processes one needs to make use of dynamical simulations, since Monte Carlo simulations are restricted to equilibrium situations only. One possible example is molecular dynamics, another is Brownian dynamics, which we used in recent work to study the problem of nucleation under shear. We used particles that interact via the Yukawa potential $V(r) = \epsilon \mathrm{e}^{-\kappa r}/\kappa r$, with r the interparticle distance, κ the inverse screening length, and ϵ the interaction strength has been fixed to $\epsilon = 1.48 \times 10^4 k_B T$. For the interaction we used a cut-off distance $r_c = 10/\kappa$. The equations of motion in Brownian dynamics also depend on the short-time diffusion constant D, and linear shear is applied via the shear rate $\dot{\gamma}$. For a more extensive description of the model we refer the reader to Refs. [5,6].

The quantity of interest is the probability $P(n)$ to find a nucleus of n crystalline particles in a super-cooled liquid. Here to all particles that belong to the crystalline nucleus need to be identified. This is done with the aid of bond-orientational order parameters, which characterize the local environment of a particle of interest. It is clear that even in the case that one applies linear time-independent shear, the quantity $P(n)$ is a well defined function in the steady state, and that it will only depend on the external pressure p, the temperature T, and the shear rate $\dot{\gamma}$. For zero shear, one can relate the function $P(n)$ to the chemical potential. It will show a maximum, which corresponds to the nucleation barrier and determines the critical nucleus size. Note that the critical nucleus size will depend on the definition that is used for the nucleus. The height of the nucleation barrier, however, should hardly be sensitive to the definition that is being used [7]. The reason is that one needs to determine the maximum cost in chemical energy for a path from a super-cooled liquid to a crystallized system. The nucleation barrier is the minimum over all possible crystallization paths of this maximum chemical energy, and does not depend on how the nucleus is defined.

Since in the presence of shear the system is not in equilibrium, the probability $P(n)$ cannot longer be related to a chemical potential. But in terms of probabilities, the critical nucleus can still be identified, since it corresponds to the least probable nucleus size.

In a conventional simulation one would prepare the system in an initial state and simulate for a number of time steps while measuring the number of particles in the nucleus. The obvious problem is that the amount of time steps in order to observe a single nucleation event will in general be astronomical, unless the nucleation barrier is very small. Moreover, once the critical nucleus size is exceeded, the nucleus will rapidly grow and crystallize the system. Therefore a large amount of simulations is required to obtain good statistical information, specially close to critical nucleus size.

We can solve this time problem with a trick. Suppose we want to measure the probability $P(n)$ close to a cluster size n_0. To do this, we need to simulate many trajectories of dynamical simulations whereby we restrict our measurements to the range of nucleus sizes

of interest. But rather than starting over and over again with a super-cooled liquid and wait until a sufficiently large nucleus is grown, we restrict the simulation to grow dynamical paths close to the preferred size n_0. This is achieved with the help of a biasing function $P_{\text{bias}}(n, n_0)$ and works as follows. We perform a normal dynamical simulation for a time that is long enough for particles to attach to or de-attach from the nucleus, but short enough so that relative small nuclei are not fully dissolved or that an over-critical nucleus crystallizes the full system. The data we obtain in such a time interval can be used for measurements. At the end of the time-interval we determine the number of particles in the nucleus n_{new} and compare that with the cluster-size n_{old} at the begin of the time interval. We now select either the original configuration or the final configuration with which we will continue the next time-interval. This selection is based on the relative probabilities $P_{\text{bias}}(n_{\text{old}}, n_0)/P_{\text{bias}}(n_{\text{new}}, n_0)$, where a suitable choice for the biasing function would be $P_{\text{bias}}(n, n_0) = \exp(-\alpha(n - n_0)^2)$ with α the strength of restrainment. A proper normalization of the biasing probability is not required, since only the relative probabilities are used.

In the conventional umbrella sampling technique, one needs to weight all measured quantities with the instantaneous Boltzmann factor due to the bias that is applied. Also in the present case we need to evaluate weighted averages. This is, however, not the instantaneous biasing probability, but the one at the begin of the time-interval, because within a time-interval the biasing function is not being used and therefore the weight should not be modified.

Fig. 1 shows a schematic representation of the general idea, which shows the size of the nucleus as function of time. The curves show dynamical paths that are generated without a bias. The bias is applied on regular time-intervals denoted by the points. The filled points represent accepted configurations and are connected by the solid curve, which forms a long-time path. The dotted curves represent short-time paths of which the final configuration (open points) are rejected by the bias, where after the most recent accepted configuration is restored. The shape of the bias ensures that the size of the nucleus is restricted, represented by the horizontal dashed lines, although excursions beyond them are allowed.

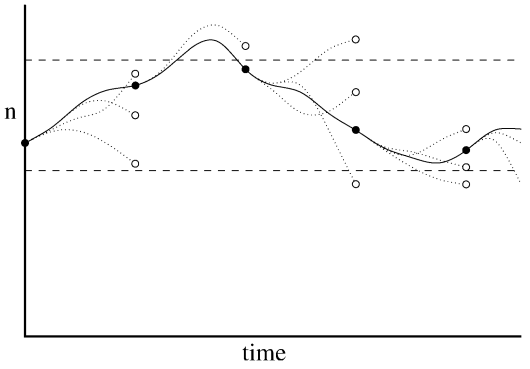

Fig. 1. Schematic representation of the umbrella sampling, which shows the size of the nucleus as a function of the time. The solid line shows the long time trajectory, while the dotted curves indicate small time-intervals. The points are configurations that are subjected to the bias and can be rejected (open points) or accepted (filled points). The bias ensures the confinement in nucleus size, which is represented by the dashed lines.

When at the end of the time-interval the original configuration is restored, one needs to ensure that the next time-interval a different path will be followed. In the case that Brownian dynamics is used, this is achieved in a natural manner by the random forces acting on the particles. For molecular dynamics this would not work, because there is no such random process available. A possible solution here would be the usage of different velocities. The usage of this method also depends critically on the assumption of the process to be Markovian, i.e. the clusters should change sufficiently in order to sample an representative part of the phase space.

The way we use the biasing function, is a simple trick to generate many appropriate initial configurations, without the necessity to generate full trajectories from the liquid state. The only problem that now remains, is to create a number of starting configurations with suitably sized nuclei. Also here we can directly make use of the same technique, because starting from the liquid we apply the biasing function with a small preferred size n_0. By slowly increasing its value, the nucleus will be forced to grow in a controlled way to any size we like to have.

For a given simulation, we keep the biasing function fixed. Therefore any quantity we measure is only obtained in a relative small range of nucleus sizes. For a measurement of the dimension of the nucleus this is not a problem, but for the determination of

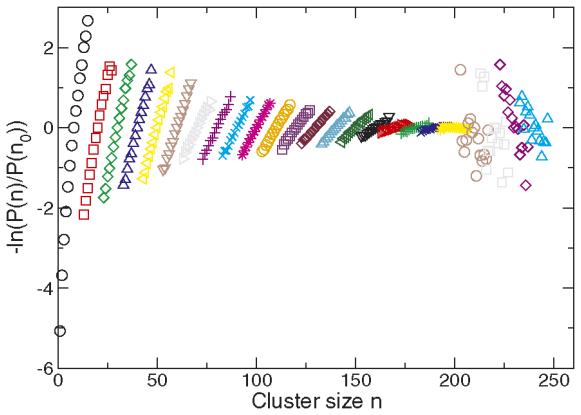

Fig. 2. The relative probability $P(n)$ of a cluster of size n with respect to the preferred cluster size n_0 stemming from the biasing function used by the umbrella sampling technique.

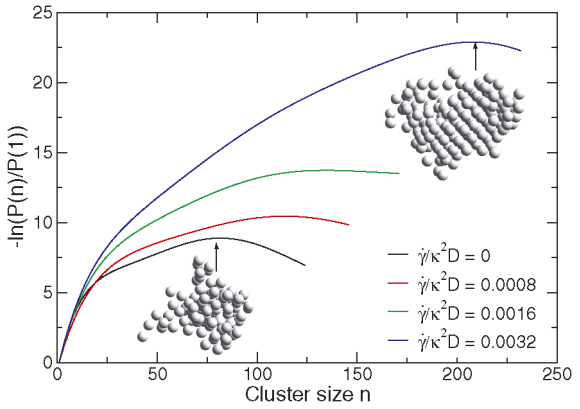

Fig. 3. Negative logarithm of the probability $P(n)$ of finding a cluster of n solid-like particles normalized by $P(1)$ for fixed dimension less pressure $\beta p/\kappa^3 = 0.24$ ($\beta = 1/k_B T$ is the inverse temperature) and different applied dimensionless shear rates $\dot{\gamma}/\kappa^2 D$. The insets show typical snapshots of critical nuclei for the largest shear rate and the zero shear case. (Taken from Ref. [6].)

the function $P(n)$ it is. The reason is simply that from a single simulation we only obtain a small part of the function. The probability measured before the acceptance criterion of the bias is applied, therefore does not have the appropriate normalization, but does give the correct relative probabilities $P(n)/P(n_0)$. By performing several simulations for different preferred cluster-sizes n_0, we obtain different overlapping patches of $P(n)$. An example of that is shown in Fig. 2, where we have plotted the negative logarithm of the function $P(n)$. The values of n_0 have been chosen to be multiples of 10 particles, and the strength α in the biasing function is chosen such that there is some overlap of successive patches. Since the overlapping parts of the patches should be identical, one is able to match all patches together with a simple fitting procedure. The result of that is shown in Fig. 3, where the negative logarithm of the function $P(n)$ is shown for different shear rates. From this figure one can understand that small shear rates lead to an increase in the critical nucleus size and a lower relative probability, hence an increase in the nucleation barrier [5,6].

3. Other applications

The method explained here can also be applied to other problems or systems. One obvious generalization is the inclusion of solvent-mediated hydrodynamic interactions in the colloidal dynamics. Another possible application is that of the problem of heterogeneous nucleation, e.g., in a sheared system confined between two plates or near a single wall [8]. In fact as far as the umbrella part is concerned, no modifications are required, and the method as outlined above can directly be used.

Let us here describe an application, which would require some modifications. Suppose one would like to investigate the process of nucleation in *oscillatory* shear [9], where the shear depends via a frequency ω on the time, i.e. $\dot{\gamma} = \dot{\gamma}_0 \sin(\omega t)$. Here, one would expect that, given a sufficient time, the system is characterized by the pressure p, the temperature T, the amplitude $\dot{\gamma}_0$, and its frequency ω. The probability function $P(n)$ of observing a nucleus of size n is also here properly defined. It is, however, important to realize that this function is a time average of the periodic, time-dependent function $P(n,t)$, caused by the fact that we do not have a time-independent steady state. In principle, the function $P(n,t)$ can be obtained in the same manner as in the case of a homogeneous shear field. The main difference is simply that we measure a two-parameter function, so if we restore an old configuration we also need to reset time and shear in the proper manner. Whether one would need to adjust the biasing function or not will depend on the chosen parameters for the oscillatory shear. For small shear, the function $P(n,t)$ will probably not depend strongly on time and a time-independent bias can still be used. In other cases it might be useful to introduce a time-dependent biasing function.

A further improvement on the simulation scheme can be obtained by using the so-called parallel tempering technique [10]. In this scheme several systems at different biasing parameters are simulated in parallel. In addition to the simulations as described before, one also allows for configurations from different biasing parameters to be swapped. The result is that nuclei that by some fluctuation grow big, will be continued with a higher biasing parameter, while nuclei that have shrunken will continue at lower preferred cluster sizes. The result is an even larger variation in configuration space, leading to better statistics.

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