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Insight into the nucleation of urea crystals from the melt

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HIGHLIGHTS

- Nucleation of urea from its melt has been simulated with Well Tempered Metadynamics.
- The nucleation FES was calculated for different system sizes and temperatures.
- A novel metastable urea crystal packing was identified.
- Multiple crystal packings coexist during the nucleation process.

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ABSTRACT

Obtaining molecular-level information regarding nucleation is an essential step towards a thorough comprehension of crystallization processes. In this work we investigate the nucleation of urea at the atomic scale using enhanced sampling Molecular Dynamics simulations. We show that by employing a set of suitably defined collective variables in a Well Tempered Metadynamics scheme it is possible to reversibly drive the system across the solid–liquid phase transition and to recover the associated free energy surface. Our study reveals the presence of an undiscovered metastable ordered structure competing with the experimental one during crystal nucleation, suggesting a non-classical mechanism for this process.

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1. Introduction

Understanding and controlling crystallization is crucial in the development of new materials as well as in the production of pharmaceuticals and fine chemicals (Doherty, 2006). Nevertheless many aspects of this transformation remain elusive. At the basis of our understanding there is Classical Nucleation Theory (CNT), which is based on a rather general description of the free energy associated with the formation of a nucleus as the sum of two terms, a favorable one, due to the lower free energy of the emerging phase, and an unfavorable surface term. An assumption of CNT is that the emerging nucleus possesses the same microscopic structure of the bulk material.

This simplified vision has been repeatedly challenged (Prestipino et al., 2012; Galkin and Vekilov, 2000; Demichelis et al., 2011) and some of its predictions have proven to be difficult to reconcile with experiments (Auer and Frenkel, 2004). Part of the challenge derives from the scale involved in nucleation; the typical radius of critical nuclei is in the nm scale and very few examples of a direct experimental characterization of the nuclei structural features and dynamical properties are available in the literature (Gasser et al., 2001; Harano et al., 2012). In contrast, computer simulations have been extensively used especially for simple model systems like Lennard-Jones or hard spheres (Auer and Frenkel, 2001; Zahn, 2004; Trudu et al., 2006; Demichelis et al., 2011; Matsumoto et al., 2002). Since nucleation takes place on a time scale that far exceeds what Molecular Dynamics can reach, these studies have been performed either by deeply quenching the system to accelerate crystallization (Trudu et al., 2006; Matsumoto et al., 2002) or by employing enhanced sampling techniques (Torrie and Valleau, 1977; Lechner et al., 2011; Laio and Parrinello, 2002).

Here we use Well Tempered Metadynamics (Barducci et al., 2008) (WTMT) to investigate the nucleation of urea, an organic molecule which, with respect to Lennard-Jones or hard spheres, presents the complication of directional interactions arising from intramolecular hydrogen bonds. This could lead to the presence

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of competing, albeit metastable, crystal structures, which could complicate the nucleation process in a way that cannot be described using CNT. It is important to highlight that providing a quantitative description of the unbiased nucleation dynamics is not an objective of this study. We rather aim at exploring the ensemble of states at increasing degrees of crystalline order that can be visited during the nucleation process. With respect to similar studies, centered on the exploration of the configurational space via Monte Carlo (Gavezzotti, 2013) simulations, we make a step further and provide an estimate of the free energy surface associated with the explored states. WTMT simulations allow us to gather a deep insight into the landscape of thermodynamically plausible crystal packings, suggesting a nucleation mechanism characterized by the competition between two crystalline phases, *i.e.* the experimentally observed urea crystal structure as well as a competing metastable polymorph.

While we do not intend to give an exhaustive description of metadynamics for which we refer the reader to the original literature (Laio and Parrinello, 2002; Barducci et al., 2008) and to a recent review (Barducci et al., 2011), we give here an introduction to the method which will enable the reader to follow the content of the paper.

2. Methods

In this work we aim at simulating urea nucleation from its melt retaining a full atomistic description. To study this problem we use molecular dynamics to simulate the collective evolution of systems consisting of thousands of atoms in which no chemical reaction is occurring. A natural choice for tackling such a problem is to use an all-atom classical forcefield. Within this framework each atom is explicitly represented and the subgroups of atoms forming molecules are defined at the beginning of the simulation. In order to model urea, we use the Generalized Amber Force Field (GAFF) (Cornell et al., 1995; Wang et al., 2004). As shown in previous works, despite its simple formulation this forcefield provides a reasonable representation of urea surfaces in contact with a solution (Salvalaglio et al., 2012, 2013). The melting temperature for the chosen urea model was estimated within the range between 400 and 420 K (Salvalaglio et al., 2012).

Performing standard MD simulations for such a system requires the numerical solution of the Newtonian equation of motion for all the interacting atoms, producing a trajectory in the configurational phase space R spanned by the Cartesian coordinates and providing the associated set of momenta at each timestep. Such a trajectory describes the evolution of the simulated system in time and provides an unbiased sampling of the configurational phase space. As mentioned in the introduction, using standard MD to sample the rare events involved in nucleation is extremely inefficient if not outright impossible due to high activation energies associated with nucleation. In order to overcome this issue we use Well Tempered metadynamics (WTMT), a state-of-the-art enhanced sampling method that allows us to improve the sampling of the phase space and recover the associated free energy surface (FES).

2.1. Metadynamics

Metadynamics is a simulation technique based on the construction of a history dependent bias potential that adaptively enhances the sampling of activated transitions. The biasing potential is built as the sum of Gaussian functions deposited in a low dimensional projection of the configurational phase space. The coordinates defining such a low dimensional space are named Collective Variables (CVs). It is important to notice that the definition of CVs is not restricted to metadynamics but is applied in combination with several other simulation techniques. CVs are in fact important not only to define a convenient space for the bias deposition but also to extract accessible and useful information from all the Cartesian coordinates computed at each timestep. Good CVs allow us to clearly identify the initial and final states associated to a given transition. Typical CVs used in crystallization problems are coordination numbers, Steinhardt parameters (Steinhardt et al., 1983; Trudu et al., 2006; Auer and Frenkel, 2001) Potential Energy (Trudu et al., 2006), tailored functions designed to maximize the symmetry within the crystal (Gavezzotti, 2013) or to describe a well determined crystal symmetry (Santiso and Trout, 2011). In metadynamics CVs are defined as continuous and differentiable functions of the Cartesian coordinates of the atoms in the system. In typical metadynamics simulations only a small number of CVs, typically less than five, is used in order to construct the biasing potential.

Plain metadynamics. In plain metadynamics (Laio and Parrinello, 2002), given a set of n CVs $S(R)=[S_1(R),\dots S_n(R)]$, where R refers to the Cartesian coordinates space of all atoms in the simulation box the instantaneous Gaussian contribution to the bias, $V(S,\tau)$ is defined as:

$$V(S,\tau)=\omega\exp\left(-\sum_{i=1}^{n}\frac{(S_i(R)-S_i(R,\tau))^2}{2\sigma_i^2}\right) \tag{1}$$

$V(S,\tau)$ is a Gaussian potential defined in the space of the CV $S(R)$, centered in $S(R,\tau)$, its instantaneous value at time τ. The two parameters ω and σ_i appearing in the expression $V(S(R),\tau)$ define the scale of the Gaussian potential added at time τ. ω is the energy deposition rate and defines the height of the Gaussian potential; σ_i is the standard deviation of the Gaussian in the S_i coordinate and defines its width, which is usually taken to be a fraction of the typical fluctuations of the CV S_i in an unbiased simulation. The total metadynamics bias at time t, $V_g(S,t)$, can thus be written as

$$V_g(S,t)=\int_0^t V(S,\tau)\,d\tau \tag{2}$$

Metadynamics allows us to estimate the free energy in the coarsened phase space defined by CVs as the negative of the deposited bias as

$$F(S)=-V_g(S,t\to\infty)+C \tag{3}$$

where C is an arbitrary constant that does not affect free energy differences between states. Converging a FES with metadynamics however is a non-trivial task for most realistic systems. It has been shown that the ΔG between two points of the CVs space computed with plain metadynamics oscillates rather than converges to a well defined value (Barducci et al., 2008; Bussi et al., 2006).

Well tempered metadynamics. Well tempered metadynamics (WTMT) (Barducci et al., 2008) is an evolution of the algorithm that allows us to reach a controlled convergence of the free energy estimates. To this aim a history dependence is introduced in the bias deposition rate ω. This is achieved by scaling the initial bias deposition rate ω_0 with an exponential function of the total bias deposited up to time τ according to the following expression:

$$\omega(S,\tau)=\omega_0\exp\left(-\frac{V_g(S,\tau)}{k_B\Delta T}\right) \tag{4}$$

in this expression $V_g(S,\tau)$ represents the total bias deposited prior to instant τ and ΔT is a parameter homogeneous to a temperature. In WTMT, the Gaussian deposited at time τ, $V(S,\tau)$ of Eq. (1) changes accordingly, as well as Eq. (2). Despite the clear analogy with plain metadynamics, the WT bias potential does actually converge to a stable estimate of the free energy in the CVs space $F(S)$, which can be recovered from the relation:

$$F(S)=-\frac{T+\Delta T}{\Delta T}V_g(S,t\to\infty)+C \tag{5}$$

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