



**Faculty of Science** 

# Nucleation of colloidal cubes using Monte Carlo simulations

Master's Thesis

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#### Abstract

In this thesis we use Monte Carlo simulations to investigate the nucleation of hard cubes and hard slanted cubes with slant angles between  $\phi = 66^{\circ}$  and  $\phi = 84^{\circ}$ . First, we examine the phase behaviour by looking at the equations of state, and find our equations of state consistent with literature. Interestingly, for smaller slant angles, the hysteresis between the two phases increases. Next, we explore the structure of both the liquid and crystal phases using the radial distribution function and the *Steinhardt* order parameter [25]. In particular, we determine local order parameters suitable for distinguishing fluid and crystal phases, based on either translational or orientational order. Finally, we examine nucleation of the simple cubic phase in a system of hard cubes. We first discuss classical nucleation theory and how nucleation rates can be determined from the free-energy barrier. To build the free-energy barrier we make use of *umbrella sampling* in Monte Carlo simulations. We present some barriers, and discuss the challenges of hard cubes nucleation. Interestingly, we found that unlike in systems of e.g. hard spheres, clusters of hard cubes do not form roughly spherical clusters.

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# 1 Introduction

In 1827, Robert Brown discovered that small particles in a fluid undergo seemingly random motion [2]. This motion, which we now call Brownian motion, is due to molecules in the solvent colliding with the particle. When these particles are small enough, the thermodynamic limit of infinitely small solvent particles does not hold up, and rather than experiencing a constant isotropic pressure, these particles visibly bounce around as fluctuations in the number of collisions are non-negligible. These particles were coined *colloids* by Thomas Graham in 1861 [13], named after the Greek word for glue ( $\kappa o \lambda \lambda \alpha$ ) because of the glue-like properties of some of these systems.

Colloids are solid particles suspended in a fluid with sizes ranging from nanometers to micrometers. In the past few decades, advancements in colloidal particle synthesis have made it possible to create a wide range of particles with different shapes and interactions [11]. One of the fascinating properties of these nanoparticles is that, because they undergo Brownian motion in a solvent, they can self-assemble into all sorts of different phases, ranging from fluids to all kinds of beautiful solid structures, see e.g. Ref. [15]. All these different particles must fill a physicist's mind with questions: What phases or structures can form? How can these be characterized? How do these system transform from one phase into the other? In particular this last question is one we look at more closely. The process of going from an isotropic liquid to an ordered crystal does not happen instantaneously. For example, in water, it is possible to *supercool* the liquid well below its freezing point [16]. This phenomenon can be explained by classical nucleation theory (CNT), which very simply but effectively describes this process: by creating a crystalline droplet inside a metastable liquid, an interface between the two phases is formed. This causes interfacial tension which costs energy. If a droplet is large enough though, the volume energy gain from being in the crystaline state surpasses the surface energy cost, and the crystal grows until it encompasses the entire system. While CNT does provide a qualitative explanation of crystal nucleation, nucleation rates derived from CNT often do not agree with experiment [9, 22].

Recently it has been suggested that that local structure in the fluid phase is an important factor for nucleation. For example, in the case of hard spheres—one of the most widely studied models of colloidal particles—it was recently found by Taffs and Royall that five-fold symmetry in the fluid phase inhibits nucleation [27]. Icosahedral arrangements of spheres, while locally efficient, inhibit further crystal growth, as five-fold symmetry does not tile space. This points us in the direction of studying structure in the liquid phase.

For anisotropic particles, there is not only translational order to take into account, but also orientational order. The question is how these types of order form, and how (and if) they interact with each other. Some research has been done by Sharma and Escobedo [23] on the topic of order formation in colloidal cubes, indicating that classical nucleation theory is a poor approximation of crystal growth in cubes. In order to better understand the nucleation process, a first step is to get quantitative measurements on the nucleation rate is by finding the free-energy barrier. This is what we will address in this thesis. To this end, we will study the nucleation of hard (slanted) cubes using Monte Carlo simulations. With the rapid increase in computing power in the last few decades, computer simulations of colloidal systems have become more and more feasible, and nowadays systems of thousands of particles can be simulated with relative ease on a normal desktop computer.

Hard (slanted) cubes form an excellent candidate for studying these types of order during the crystallization process for a few reasons. Firstly, the phase behaviour of hard (slanted) cubes is well known as it has been studied in the past [4, 24], and we know that hard cubes go from a disordered liquid to a simple cubic crystal with both translational as well as orientational order. Therefore we can use the knowledge of the phase boundary to study the question of how the two types of order interact with each other directly, rather than first having to determine the possible crystal structures that could form. Secondly, hard (slanted) cubes are very easy to model and therefore are also not too computationally expensive to simulate. Lastly, colloidal cubes are already possible to make relatively easily, and out of various different materials such as silver [26], gold [14, 26], platinum [19], and palladium [7], whose 3D structures can be examined in real space using e.g. electron microscopy. The end goal of thesis is to calculate the free-energy barriers from CNT. To do this, this thesis is divided into three parts: in Part I we introduce the model and compare the equations of state we find with literature to confirm that our simulation is working as intended; in Part II we explore the structure of the fluid in two ways. Firstly using the radial distrubution function to examine the lengthscale of the local environment in both the fluid and the crystal phases; and secondly we investigate how to distinguish both translation and orientational ordered particles from disordered liquid particles, for which we will use the *Steinhardt* order parameter [25]; in Part III we finally discuss nucleation theory, where we go into more detail on classical nucleation theory and employ *umbrella sampling* to obtain free-energy barriers.

# Part I

# Introduction to Modelling and Phase Behaviour of Hard 'Slanted' Cubes

In this Part we will first introduce the model in Section 2.1, and explain how we detect overlap between cubes using the separating axis theorem in Section 2.1.1. We will also cover the basics of Monte Carlo simulation in Section 2.2. Then in Section 3 we examine equations of state for a range of slant angles and compare them to literature to see if our simulation is working as intended.

# 2 Hard 'Slanted' Cubes Model and Basic Simulation Details

#### 2.1 Model

We consider hard cubes of edge length  $\sigma$ . We will also consider cubes with a *slant angle*  $\phi$ , formally called *right rhombic prisms*, but we will always refer to them as 'slanted cubes.' A sketch of a slanted cube is shown in Figure 1. We will consider slant angles  $\phi = 90^{\circ}$  (cubes) to  $\phi = 66^{\circ}$ , as in Ref. [4]. Every side length in a slanted cube is also equal to  $\sigma$ . Note that we do not consider slanted cubes with smaller slant angles, as their phase behaviour is significantly different than for larger slant angles. See Ref. [3] for more details.



Figure 1: A slanted cube with a slant angle  $\phi$ .

We assume all interaction potentials are hard. With a 'hard' interaction slant angle we mean that (slanted) cubes have no attraction or repulsion, except for

an infinite energy cost for overlap, effectively forbidding this according to the Boltzmann distribution. That is, the interaction energy  $U_{\text{pair}}(i, j)$  from a pair of cubes i and j is given by

$$U_{\text{pair}}(i,j) = \begin{cases} \infty & \text{if } i \text{ and } j \text{ overlap,} \\ 0 & \text{otherwise.} \end{cases}$$
(1)

This model has been studied extensively before, see e.g. Refs. [4, 23, 24] and we know that at low density the system forms a liquid which is both disordered translationally as well as orientationally. For both cubes and slanted cubes at sufficiently high density, the system exhibits a simple cubic crystal structure with the appropriate orientational order. For slanted cubes, there is a phase at even higher density, known as the *rhombic crystal*. In this phase the cubic orientation symmetry is also lost and all slanted cubes have the same orientation. We will, however, not investigate the rhombic crystal phase. In Ref. [24] it was shown that cubes form a crystal with many vacancies, much more than in e.g. a system of hard spheres. Later it was also found that the same vacancies are found in systems of slanted cubes, regardless of slant angle [4]. We will not investigate these vacancies either.

#### 2.1.1 Separating Axis Theorem

In this thesis we investigate the nucleation behaviour of (slanted) cubes using Monte Carlo simulations. In order to do this we require a way to determine the interaction potential in Eq. 1. Hence, we need to be able to detect when two (slanted) cubes overlap. In order to check for overlap between cubes, we use the *separating axis theorem* [12], which can be applied in general to determine whether any two convex polyhedra are separated. The idea is as follows. Given two objects in 3D space, whenever we can find a plane that separates the two objects, we are sure that the two objects do not overlap. On the other hand, if there exists no such plane, then given that the two objects are convex, we must conclude the objects overlap. We can efficiently check that two objects are separated by a plane by projecting the objects on an axis normal to the plane. If we can find a *separating axis*, such as in Figure 2a, i.e. an axis on which the projections of the objects overlap on every axis however, the objects must overlap, like in Figure 2b.

Finding a separating axis is sufficient for concluding the two objects do not overlap, but how many, and which axes must we check before we can conclude the two objects must overlap? It is proven in Ref. [12] that the axes defined by the following vectors are sufficient to conclude that the objects must overlap:

- The normal vectors of each face of the first object,
- The normal vectors of each face of the second object,
- All cross products  $a \times b$  where a is an edge<sup>1</sup> of the first object and b is an edge of the second object.

 $<sup>^{1}</sup>$ Strictly speaking, an edge has no direction, so an edge defines two vectors. However we do not care about the direction since we use this vector to define an axis.



Figure 2: An illustration of the separating axis theorem. (a) A separating axis for the blue and orange square. (b) Overlapping objects have no separating axis.

In the case of slanted cubes, we can take advantage of symmetry to reduce computation time. A slanted cube only has three differently oriented faces, and also only three differently oriented edges. This means that, to check for overlap between two slanted cubes, we only need to check the six normals on the faces of the cubes, and take every combination of cross products between one edge from the one cube and one edge from the other. As a result, we need to check  $6 + 3 \times 3 = 15$  axes. If and only if all axes fail to show separation, we can conclude that the cubes overlap.

#### 2.2 Monte Carlo Simulation

We now give a very brief overview of Monte Carlo (MC) simulations following Ref. [5]. A full description of how to implement MC simulations can be found in Ref. [10]. The main goal of a MC simulation is to approximate ensemble averages such as

$$\langle A \rangle = \frac{\int d\mathbf{r}^N A(\mathbf{r}^N) \exp[-\beta U(\mathbf{r}^N)]}{\int d\mathbf{r}^N \exp[-\beta U(\mathbf{r}^N)]},\tag{2}$$

where  $\beta = 1/k_B T$  is the inverse temperature,  $U(\mathbf{r}^N)$  is the total internal energy, and A is some observable. In principle we could calculate this by numerically integrating this expression over all of phase space (in this case all possible positions of all N particles). However it quickly becomes apparent that when we have any reasonable number of particles in our system, the phase space becomes simply too large to sum over. Instead, if we could sample states  $\{\mathbf{r}_1^N, \mathbf{r}_2^N, \ldots\}$  according to a desired distribution, in this case the Boltzmann distribution  $e^{-\beta U(\mathbf{r}^N)}$ , then after M samples our estimate of the ensemble average reduces to simply

$$\langle A \rangle = \frac{1}{M} \sum_{i=1}^{M} A(\boldsymbol{r}_{i}^{N}), \qquad (3)$$

the average of our measurements. In order to obtain accurate ensemble averages, we want to create as many configurations as possible with probabilities according to the Boltzmann distribution. The standard way of doing this is by using a *Markov process*. We follow Ref. [21]. The idea is that we only generate one initial configuration, and use this configuration to generate a new one, and use this to generate the next, et cetera so we get a *Markov chain* of states. We do this using a special process chosen such that in the end, we generate states with probabilities according to the Boltzmann distribution. We also place two further restrictions on our Markov process. First, the condition of *ergodicity*, that is, we require that in principle we could reach any state of the system from any other state, given we simulate for long enough. We do this since we do not want to arbitrarily cut off portions of phase space by starting in a certain configuration. The second condition is that of *detailed balance*, which ensures that we get the Boltzmann distribution at equilibrium. The condition of balance is the defining characterstic of equilibrium: the rate of going in and out of any state to any other state must be equal. But for reasons described in Ref. [21] we require the stronger condition of *detailed* balance: the rate of going from any state to any other state must be equal. That is, for any two states  $\mu$  and  $\nu$ ,

$$p_{\mu}P(\mu \to \nu) = p_{\nu}P(\nu \to \mu),$$

where  $p_{\mu}$  is the probability of the system being in state  $\mu$ , and  $P(\mu \rightarrow \nu)$  is the probability that the Markov chain chooses to go to state  $\nu$  from state  $\mu$ .

The MC simulation that we use in this thesis is a standard algorithm whose details are clearly described in Ref. [10]. In short, we initialize a system in a box at a specific density in a specific phase. Because we are not interested in surface effects, we use periodic boundary conditions. We then perform MC 'moves.' These moves can consist of simply a translation of a randomly chosen particle, a rotation of a randomly chosen particle, or a rescaling of the box volume. The acceptance criteria for these moves is the standard Metropolis acceptance given in Ref. [10]. Note that the volume changes are only included when we are interested in the NpT ensemble.

#### 2.2.1 Cell Lists

As in this study we need to examine large system sizes, the efficiency of our overlap check is important. In order to speed up simulations, especially those with a large number of cubes, we employ *cell lists*. After moving or rotating a cube, we need to check for overlap. Naively we can do this by simply checking for overlap with each other cube. However, in a system with thousands of cubes, most of the cubes are very far away and do not need to be checked. In order to not have to check every cube, but check only neighbouring cubes, we divide the system up into a grid of cells as shown in Figure 3. We keep track of which cells the cubes are in, and update the cell list when a cube moves to another cell. If we keep the cells large enough (that is, with a side length larger than the circumscribed sphere of our particles), we only need to check for overlap with cubes in the cube's own and neighbouring cells. This scales well with system size, as the number of cubes we need to check collision with stays constant as the number of cubes increases.



Figure 3: The advantage of using a cell list. When the red cube makes a move, it only needs to check for overlap with cubes in the same and neighbouring cells, shaded in grey.

# 3 Phase behaviour

In this Section we examine equations of state for a range of slant angles and compare them to literature to see if our simulation is working as intended. By running multiple NpT ensembles for differing pressures p, and finding the equilibrium density  $\rho$  for each p, we can find the equation of state. This has been done before for both cubes [24] and slanted cubes [4], and we will compare our results to previously done research to see if the simulation is working as intended.

For slant angles ranging from  $\phi = 90^{\circ}$  (cubes) to  $\phi = 66^{\circ}$ , two runs have been done per pressure: a compression run, starting at a relatively low density of  $\rho\sigma^3 = 0.4$  (i.e. in the fluid phase), and a melting run, starting in a relatively high density of  $\rho\sigma^3 = 0.6$  (i.e. in the crystal phase). Both runs start with  $N = 12^3 = 1728$  cubes on a simple cubic lattice, but in the compression run this crystal melts immediately because of the low density. The result for cubes is shown in Figure 4. Specifically, in Fig. 4a we show the equation of state for a larger range of pressures, and in Fig. 4b we present a more detailed look at the interesting region around the phase boundary. We can compare Fig. 4b with Fig. 5, from Ref. [24], where the equation of state is shown for both the simple cubic crystal with vacancies (light grey) and without vacancies (dashed, dark grey). We did not examine this difference as it has a relatively minor effect on the equation of state. Nevertheless we find good agreement.



Figure 4: The equation of state of hard cubes over (a) a large density range and (b) A zoom-in around the phase transition.

From the equation of state of cubes (Fig. 4b), we see that a phase transition occurs somewhere between a dimensionless pressure of  $\beta p \sigma^3 = 5.9$  and  $\beta p \sigma^3 = 6.2$ . This is consistent with the earlier result from Ref. [24] that finds a coexistence pressure of  $\beta p \sigma^3 = 6.16$ . The turning point from the low density liquid phase to the higher density crystal phase is different in the melting and compression runs, because in the compression runs the cubes start in a fluid, and the system needs to overcome the free-energy barrier that will be discussed in Section 6.1, which we will attempt to construct in Section 7.2. This difference between turning points from the liquid to crystalline phase and backwards is typical of first-order phase transitions and is referred to as *hysteresis*.

The equation of state for slanted cubes (i.e. with a slant angle  $\phi = 84^{\circ}$  to  $\phi = 66^{\circ}$ ) can be found in Figures 6–9, where we again show both a larger range of pressures, and a more detailed look at the transition between the liquid and crystalline phase.

When we compare the equation of state of hard cubes (Fig. 4) to that of other slant angles (Fig. 6–9), we notice two trends: Firstly, as the slant angle decreases, the pressures at which the system forms a crystal rises. Secondly, as the slant angle decreases, the hysteresis observed from the difference between the compression run and the melting run increases. The first trend can be interpreted as that cubes with a smaller slant angle



Figure 5: The equation of state for cubes made by Smallenburg et al. taken from Ref. [24]. The light grey line corresponds to the simple cubic crystal with vacancies, the dashed darker grey line corresponds to the simple cubic crystal without vacancies.



Figure 6: The equation of state of hard slanted cubes with a slant angle of  $\phi = 84^{\circ}$  over (a) a large density range and (b) A zoom-in around the phase transition.

are harder to push together into a crystal. This makes sense, as the more slanted a cube is, the less nicely it fits in a cubic box, which is the space that a particle in a simple cubic crystal effectively has. The second trend suggests that the free-energy barrier between the liquid and crystalline phases is higher for smaller slant angles, which can be due to a higher surface tension between the two phases, a lower bulk energy gain from the crystal phase, or the shape of the particles somehow impedes the crystal phase growth. We also compared the equations of state with those found in Ref. [4] and found good agreement. In conclusion these results give us a good picture of where phase transition between the liquid and the simple cubic crystal phase occurs in this system, which will be useful in the remainder of this report.



Figure 7: The equation of state of hard slanted cubes with a slant angle of  $\phi = 78^{\circ}$  over (a) a large density range and (b) A zoom-in around the phase transition.



Figure 8: The equation of state of hard slanted cubes with a slant angle of  $\phi = 72^{\circ}$  over (a) a large density range and (b) A zoom-in around the phase transition.



Figure 9: The equation of state of hard slanted cubes with a slant angle of  $\phi = 66^{\circ}$  over (a) a large density range and (b) A zoom-in around the phase transition.

# Part II Structure Characterization

In this part we explore a number of different ways to characterize the local 'crystalline' structure in the fluid. First, in Section 4 we explain the methods we will be using. In particular, in Section 4.1 we examine the radial distribution function, and in Section 4.2 we study the local translational as well as local orientational order to determine local crystallinity. Then, in Section 5, we apply these methods to the case of both hard cubes and hard slanted cubes. In particular, in Section 5.1 we measure the radial distribution function for both the fluid and crystal phase, for hard cubes and a variety of slant angles. In Section 5.2 we then apply the methods of detecting crystalline order using translational and orientational order parameters to make a distinction between the crystal and liquid phase.

## 4 Theory

#### 4.1 Radial Distribution Function

A simple way to look at the structure in a colloidal system is to look at the radial distribution function g(r). The g(r) can be used to get an idea of characteristic distances that appear in a system, and is often used to find the nearest neighbours, often referred to as the first-neighbour shell.

To define the radial distribution function, we start by introducing the pair correlation function  $\rho^{(2)}(\mathbf{r},\mathbf{r}')$ , which is the probability that there is a particle at position  $\mathbf{r}$  and  $\mathbf{r}'$  at the same time. Formally, the pair correlation function is defined as [5]

$$\rho^{(2)}(\boldsymbol{r},\boldsymbol{r}') = \left\langle \sum_{i} \sum_{j \neq i} \delta(\boldsymbol{r} - \boldsymbol{r}_{i}) \delta(\boldsymbol{r}' - \boldsymbol{r}_{j}) \right\rangle.$$
(4)

where  $\langle \cdot \rangle$  denotes the ensemble average,  $\mathbf{r}_i$  is the position of particle *i*, the sums are over all pairs of particles and  $\delta$  is the Dirac delta function. If the system is homogeneous and isotropic, then this function only depends on the distance between the particles. These simplifications lead to the radial distribution function g(r) [5]

$$\rho^{(2)}(\mathbf{r}, \mathbf{r}') = \rho^2 g(|\mathbf{r} - \mathbf{r}'|), \tag{5}$$

where the density  $\rho$  of particles in the system has been factored out. This is done so that g is dimensionless and  $g(r) \to 1$  as  $r \to \infty$ .

Looking at Equation 5, the radial distribution function goes to 1 in the limit of low densities. Additionally, for simple cubic crystals, like the ones formed by (slanted) cubes, we expect to see peaks in the radial distribution function at distances between simple cubic lattice sites, so at distances  $a, \sqrt{2}a, \sqrt{3}a, 2a$  et cetera where a is the lattice constant.

#### 4.2 Order Parameter

In this Section we will discuss the Steinhardt *bond-orientational* (or simply translational) order parameter which is commonly used in the detection of crystalline order [4, 18, 20, 23, 25]. Aside from translational order, we also consider orientational order, because we are studying cubes which have an orientation.

#### 4.2.1 Translational order parameter

First we discuss the Steinhardt order parameter in general. For a nonnegative integer  $\ell$  and integers  $|m| \leq \ell$ , we define for cube *i* the local translational order parameter [25]

$$q_{\ell,m}(i) = \sum_{j} Y_{\ell,m}(\theta_{i,j}, \phi_{i,j}),$$
(6)

where the sum is over all neighbours of cube i,  $\theta_{i,j}$  and  $\phi_{i,j}$  are the polar angle and the azimuthal angle of the vector from cube *i*'s centre to cube *j*'s centre, respectively, and  $Y_{\ell,m}$  are the spherical harmonics. The translational correlation between neighbouring cubes *i* and *j* is then defined by taking the dot product and normalizing [23]:

$$d_{q_{\ell}}(i,j) = \frac{\sum_{m=-\ell}^{\ell} q_{\ell,m}(i) \cdot q_{\ell,m}^{*}(j)}{\sqrt{\left(\sum_{m=-\ell}^{\ell} |q_{\ell,m}(i)|^{2}\right) \left(\sum_{m=-\ell}^{\ell} |q_{\ell,m}(j)|^{2}\right)}}.$$
(7)

Here the asterisk stands for complex conjugation. This translational correlation between two cubes will be a number between -1 and 1, which correspond to perfect anti-ordering and ordering respectively. Because the systems we will be studying form a simple cubic crystal, we choose to restrict our attention to the  $\ell = 4$  case, as it has been observed that  $q_4$  captures simple cubic order well [20, 25].

#### 4.2.2 Orientational order parameter

For orientational order we do something similar to the translational order case, but we need to take into account the symmetries of the cube. To this end, we define three vectors for each cube: the three unit vectors perpendicular to one of the faces of the cube and each other. This definition is ambiguous, as for each face, there are two unit vectors (i.e. one pointing inward, the other pointing outward). However because we will consider only even- $\ell$  spherical harmonics, which are invariant under inversion [25], this distinction disappears. For slanted cubes, there is a choice to make. The three vectors defined above could equivalently be defined as 'the edges of the cube.' If we consider cubes with a slant angle smaller than 90°, these two definitions would differ. This difference, and an alternative definition have been studied and will be discussed in Section 5.2.2. Just like with the translational order parameter, in general for a nonnegative integer  $\ell$  and integers  $|m| \leq \ell$ , we define for cube j the local orientational order parameter [6]

$$i_{\ell,m}(j) = \frac{\sum_{n=1}^{3} Y_{\ell,m}(\theta_n(j), \phi_n(j))}{\sqrt{\sum_{m=-\ell}^{\ell} |\sum_{n=1}^{3} Y_{\ell,m}(\theta_n(j), \phi_n(j))|^2}}.$$
(8)

Here the sum over n means the sum over the three axes defined above,  $Y_{\ell,m}$  are again the spherical harmonics, and now  $\theta_n(i)$  and  $\phi_n(i)$  are the polar angle and the azimuthal angle of the vector n of cube j, respectively. Now again, we define the correlation between neighbouring cubes j and k by taking the dot product, where normalizing has already been done in the last step, so we define [23]

$$d_{i_{\ell}}(j,k) = \sum_{m=-\ell}^{\ell} i_{\ell,m}(j) \cdot i_{\ell,m}^{*}(k).$$
(9)

Just like with the translational correlation, this will be a number between -1 and 1, corresponding to perfect anti-ordering and ordering respectively. As with the translational order case, because the systems we will be studying form a simple cubic crystal, we will restrict our attention to the  $\ell = 4$  case, as we expect that orientational order will also be captured well by  $i_4$ .

#### 4.2.3 Ordered Bonds, Cubes, and Clusters

For both types of order, having defined the order parameter for each cube as well as the order correlation between two cubes, we define a few terms which we will be using throughout this thesis. We define a 'cutoff radius,' and say that two cubes within that cutoff radius have a *bond*. If the order correlation of two bonded cubes is above an 'order cutoff,' we say that two cubes have an *ordered bond*. Next we define a cube to be an *ordered cube* if it has at least four ordered bonds, and finally a *cluster* is a collection of at least three ordered cubes which are connected in the sense that they share ordered bonds.

From a visualization perspective, a nice trick to visualizing clusters is by showing particles which belong to a cluster in their true size, while showing all non-ordered cubes at only a fraction of their true size, so we can 'see through' them. An example of what a fluid filled with some clusters of crystallinity might look like can be seen in Figure 10. We will always colour different clusters in a different colour, unless there are too many different clusters.



Figure 10: A typical snapshot of a liquid of cubes, with different clusters colored differently, and all non-crystalline cubes drawn small.

## 5 Measurements

### 5.1 Radial Distribution Function

We begin our study of the structure of the fluid by examining the radial distribution function in fluid phases for cubes for a range of densities from about  $\rho\sigma^3 = 0.35$  to  $\rho\sigma^3 = 0.45$ . We choose these densities because they are below the liquid-crystal coexistence densities of cubes. The radial distribution functions can be seen in Figure 11. We see that there are no cubes within a distance of  $\sigma$ , which is as expected, because we do not allow cubes to overlap. Furthermore, we see the shell structure typical of a liquid, as the density is high at around  $r = 1.4\sigma$ , then low at  $r = 2.1\sigma$ , then high again at  $r = 2.8\sigma$  etc. The first minimum after the peak signifies the end of the first shell. We also see that as the density increases, the intensity of the second and third shell increase, and the shells become slightly thinner.



Figure 11: The g(r) of systems of N = 1728 cubes over a range of pressures resulting in a range of densities from  $\rho\sigma^3 = 0.35$  to  $\rho\sigma^3 = 0.44$ . Note the first minimum is marked in every plot.

To see how much the particle shape influences the first shell, we now examine the g(r) for a range of slant angles from  $\phi = 84^{\circ}$  to  $\phi = 66^{\circ}$ . The distribution functions can be found in Figure 12. As we can see, the distribution function changes only slightly. As the slant increases, the first minimum moves to slightly lower r, from  $2.1\sigma$  at  $\phi = 90^{\circ}$  (Figure 11d) to  $2.0\sigma$  at  $\phi = 66^{\circ}$  (see Figure 12d). Furthermore, the intensity of the shells decreases, as the maximum of the g(r) is almost 2 for cubes (see Figure 11d), but only 1.7 for cubes with a slant angle of  $\phi = 66^{\circ}$ . It is important to note that the density also decreases, even though the pressure remains the same. This decrease in density could also partly explain the lower peaks in the density profile.



Figure 12: The g(r) of systems of N = 1728 slanted cubes over a range of slant angles from 66° to 84°. Note the first minimum is marked in every plot.

The first neighbour shell of the fluid and crystal is expected to vary somewhat. Hence, we now explore the g(r) for the crystal for cubes with a slant angle from  $\phi = 66^{\circ}$  to  $\phi = 90^{\circ}$  (cubes). See Figure 13 for the radial distribution functions found for these slant angles. As seen in Figure 13, the crystal g(r) exhibits a number of clear peaks, that correspond roughly to the distances between lattice sites in the simple cubic lattice<sup>2</sup>. Moreover, the first peak is much narrower, and there is a clear distinction between nearest neighbours and second and third nearest neighbours, unlike in the liquid case. We see that as the slant increases, this distinction diminishes, as the first and second nearest neighbour distributions overlap much more. From these plots, we can infer that most first neighbours are within a distance of  $1.4\sigma$ , regardless of slant angle, although it must be noted that the density for each slant angle is slightly different. To find the distance of the first neighbour shell of cubes at the highest density of a liquid ( $\rho\sigma^3 = 0.45$ )[4], we use that the lattice constant scales as  $a \sim \rho^{-1/3}$ . Then we find that in the liquid of cubes, the first neighbours should be within a distance of  $1.4\sigma (0.45/0.58)^{-1/3} \approx 1.52\sigma$ . This result will be used in the next Section.

 $<sup>^{2}</sup>$ Note that except for the first peak, all other peaks are combinations of peaks from different lattice-site distances.



Figure 13: The g(r) of systems of N = 1728 slanted cubes over a range of slant angles from  $\phi = 66^{\circ}$  to  $\phi = 90^{\circ}$  at higher pressure. Note the first minimum is marked in every plot. Also note that for smaller slant angles, the pressure was increased to keep the density somewhat similar.

#### 5.2 Order Parameter

In this Section we will use the order parameters  $q_4$  and  $i_4$  to differentiate the crystal phase from the liquid state. In particular, in Section 5.2.1 we examine the order parameter distributions on a global level to determine the order cutoff  $d_{\rm cut}$  used for classifying cubes as ordered. In Section 5.2.2, we address the ambiguity of the definition of orientational order for slanted cubes.

#### 5.2.1 Global order distributions

In Section 5.1 we determined that the first neighbours in a simple cubic lattice at a density of  $\rho\sigma^3 = 0.45$  should be within a distance of  $1.52\sigma$ . Because this value is close to our preliminary value of  $1.55\sigma$  that we used, the result justifies this value and we therefore call all cubes within a distance of  $1.55\sigma$  bonded. In order

to determine a proper cutoff  $d_{\text{cut}}$  for what bonds we consider to be *ordered*, we set up an NpT simulation with N = 8000 cubes which starts in a low density disordered liquid and set the pressure very high to 'crush' the system to a high density crystal. When the system reaches densities of  $\rho\sigma^3 = 0.40$  to  $\rho\sigma^3 = 0.55$  in steps of 0.01, we record the  $d_{q_4}$  and  $d_{i_4}$  order correlation distributions, both the total distribution as well as the distribution of order correlation averaged per cube. These can be found in Figure 14. Typical snapshots from both liquid and crystal configurations can be Figure 15.



(a) Distribution of translational order correlation.



(c) Distribution orientational order correlation.



(b) Distribution of translational order correlation averaged per cube.



(d) Distribution orientational order correlation averaged per cube.

Figure 14: The translational as well as orientational order distribution ranging from a low density fluid to a high density crystal. An NpT simulation of N = 8000 cubes starting at a density of  $\rho\sigma^3 = 0.1$  was run at a very high pressure of  $\beta p\sigma^3 = 10000$ . When the density reaches  $\rho\sigma^3 = 0.4, 0.41$  et cetera, the translational and orientational order is calculated for all bonds. On the left the total distribution is plotted, on the right the distribution of the average order for per cube is plotted.

In Figure 14 we see a clear difference between the distribution of a low density liquid and a high density crystal. In Figures 14a and 14c, we see that as the density increases, more of the system becomes crystalline, as the distribution shifts from a broad range centered around  $d_{q_4} = 0.3$  and  $d_{i_4} = 0.1$  to a narrow distribution around  $d_{q_4} = d_{i_4} = 0.85$ . The distinction between these distributions is even more obvious in Figures 14b and 14d, where the correlations have been averaged per cube. These last results are especially powerful for discerning crystalline cubes from liquid ones. This can be explained by the fact that in a liquid, order correlations are distributed more or less randomly. So, if we average a number of bonds, we are more likely to end up with a number closer to the center of the distribution. Interesting to note is that though the liquid is mostly disordered, there is a slight net positive amount of order in the liquid phase, which is more pronounced in the translational order. Also noteworthy is that for both the translational and orientational order, even for the order averaged per cube, the distribution seems to shift continuously from low order to higher order, rather than seeing the 'liquid' distribution shrink and the 'crystal' distribution grow. This is likely due to cubes in the interface between crystal and the liquid, which have an intermediate amount of order.

From Figures 14b and 14d we can infer that in the liquid phase (densities  $\rho\sigma^3 < 0.45$ ), almost no cubes have an average translational bond correlation with their neighbours of more than 0.6, and no average orientational bond correlation of more than 0.5. With these results we can set the bond order parameter cutoff to  $d_{\rm cut} =$ 0.6. Any correlation larger than  $d_{\rm cut}$  will be considered an ordered bond.



Figure 15: Two snapshots of the system consisting of 8000 cubes. (a) The system at a density of  $\rho\sigma^3 = 0.40$ , resulting in a fluid. (b) The system at a density of  $\rho\sigma^3 = 0.55$ , resulting in a crystal.

#### 5.2.2 Orientational Order Parameter for Slanted Cubes

In Section 4.2.2, we mentioned an ambiguity in defining the orientational order axes used to calculate the orientational order in slanted cubes. For a given cube, we defined three axes, namely the normal vectors on each face of the cube. These coincide with the edges of the cube. For cubes with a slant angle of less than  $\phi = 90^{\circ}$  however, these two definitions will give different sets of vectors. Actually, the one set is just a rotated version of the other, which should give us the same results because the order parameter we use is rotationally invariant [25]. Alternatively, we can consider the normal vectors defined by the normal vectors on the faces of the 'unslanted cube.' That is, we consider the slanted cube to be not slanted. Given the symmetries of the slanted cube, there are actually two ways to 'unslant' the cube, so by picking one we break the symmetry of the slanted cube<sup>3</sup>.

We will now investigate how the choices of these vectors affect the ability to measure orientational order. In order to do so, we do the same simulation as in the previous Section, but with slanted cubes with a slant angle of  $\phi = 72^{\circ}$ . That is, we ran an NpT simulation with N = 8000 slanted cubes which start in a low density disordered liquid and set the pressure very high to 'crush' the system to a high density crystal. When the system reaches densities of  $\rho\sigma^3 = 0.40$  to  $\rho\sigma^3 = 0.55$  in steps of 0.01, we record the  $i_4$  order distributions, calculated using the three different sets of orientation vectors described above. The results can be found in Figure 16. From these figures we can see that all of the methods give us very similar results. Though we expected the methods using slanted face normals (Fig. 16c and 16d) and edges of the slanted cube (Fig. 16e and 16f) to be similar because the vectors they define are a simply a rotated version of each other, we can also see that using unslanted edges (Fig. 16a and 16b) has nearly identical results. We thus conclude that the difference between calculation orientational order from the different sets of three vectors does not matter.

 $<sup>^{3}</sup>$ One could argue that therefore this is a flawed choice. We will nevertheless explore this option.



(a)  $d_{i_4}$  distribution using unslanted face normals.



(c)  $d_{i_4}$  distribution using using slanted face normals.

probability density



(b)  $\overline{d_{i_4}}$  distribution using unslanted face normals.



(d)  $\overline{d_{i_4}}$  distribution using slanted face normals.



Figure 16: The orientational order distribution of a system of N = 8000 slanted cubes with a slant angle of  $\phi = 72^{\circ}$  over a density from  $\rho\sigma^3 = 0.4$  to  $\rho\sigma^3 = 0.55$ . In (a) and (b) the order was calculated using the unslanted cube face normals, in (c) and (d) using the slanted cube face normals, and , in (e) and (f) using the edges of the slanted cubes. Note that the scale on the vertical axis is not the same in each plot.

# Part III Nucleation of Hard Cubes

In this Part we finally examine the nucleation of cubes. First we will explain some theory and methods in Section 6. In particular, in Section 6.1 we discuss the simplest model for nucleation, called classical nucleation theory (CNT). There we will delve into nucleation barriers, which can used to determine for example the nucleation rate, which we will derive in Section 6.2. We will then discuss how to study rare-event nucleation using umbrella sampling in Section 6.3. Then, we will apply these methods in Section 7. In particular in Section 7.1 we explain how we created a metastable liquid necessary to investigate nucleation. In Section 7.2 we then use this metastable liquid to go from a cluster size distribution to a piece of the free-energy barrier, and then put the pieces together to construct the complete free-energy barrier. We then explore how different parameters affect the barrier.

## 6 Theory

#### 6.1 Classical Nucleation Theory

The simplest model of nucleation is well known, and goes by the name of classical nucleation theory (CNT). The theory applies when we have a system in a *metastable* state. The idea is as follows. The entire system of interest is in state A with a chemical potential  $\mu_A$ , but under current conditions (due to e.g. pressure, density) the Gibbs free energy of the system would be lower in state B, with a chemical potential  $\mu_B < \mu_A$ . However, by changing a droplet in the system from state A to state B, we create an interface between state A and state B with surface tension  $\gamma > 0$ . See Figure 17 for a sketch of the system. CNT generally asserts that a droplet is spherical (which makes sense, as this gives the most volume for the least area), so the energy change from a droplet with radius r will be

$$\Delta G(r) = 4\pi r^2 \gamma - \frac{4\pi r^3 \rho_B \Delta \mu}{3}, \qquad (10) \quad \text{Fig}$$

в

Α

Figure 17: A cartoon of the system described by CNT.

where  $\Delta \mu = \mu_A - \mu_B > 0$  is the supersaturation, and  $\rho_B$  is the density of phase *B*. Naturally, if making the droplet larger makes this energy cost greater, i.e. if  $\frac{d\Delta G(r)}{dr} > 0$ , then the system will, in order to minimize the Gibbs free energy, make the droplet smaller. However, because  $r^3$  grows faster than  $r^2$ , at sufficiently high *r* the bulk free-energy gain will overtake the surface free-energy cost. This can be easily calculated by setting the derivative to zero, and we find the critical droplet radius

$$r^* = \frac{2\gamma}{\rho_B \Delta \mu}.\tag{11}$$

This results in a free-energy barrier of

$$\Delta G(r^*) = \frac{16\pi\gamma^3}{3\rho_B^2 \Delta\mu^2}.$$
(12)

### 6.2 Nucleation Rate

To obtain the nucleation rate in terms of the free-energy barrier from classical nucleation theory, we follow Ref. [29] and Ref. [1]. Here we assume that the clusters of phase B grow and shrink by attaching and removing a single particle respectively<sup>4</sup>. We define the flux of nuclei going from size n to n + 1 as [29]

$$R_n = N_n k_{+,n} - N_{n+1} k_{-,n+1}, \tag{13}$$

where  $N_n$  is the number of clusters of size n and  $k_{\pm,n}$  are the attachment (+) and detachment (-) rate of a single particle to a cluster of size n. In equilibrium, there is no net flux. We can use this to eliminate  $k_{-,n}$  from Eq. 13, to get

$$R = k_{+,n} N_n^{\rm eq} \left( \frac{N_n}{N_n^{\rm eq}} - \frac{N_{n+1}}{N_{n+1}^{\rm eq}} \right), \tag{14}$$

where R is the steady-state nucleation rate which is equal for all cluster sizes, and  $N_n^{\text{eq}}$  is the equilibrium cluster size distribution, for which we will make some assumptions. First, for cluster sizes smaller than the critical nucleus size (i.e.  $n \ll n^*$ ), the steady state distribution is approximately equal to the equilibrium distribution, so  $N_n^{\text{eq}} \approx N_n$ . Secondly, for  $n \gg n^*$ , the steady state distribution will go to zero while the equilibrium distribution does not, so  $N_n^{\text{eq}} \ll N_n$ . We now use these assumptions in Eq. 14 after dividing by  $k_{+,n}N_n^{\text{eq}}$  and sum over cluster sizes from  $L \ll n^*$  to  $H \gg n^*$ . We get

$$R\sum_{n=L}^{H} \frac{1}{k_{+,n}N_n^{\text{eq}}} = \sum_{n=L}^{H} \left(\frac{N_n}{N_n^{\text{eq}}} - \frac{N_{n+1}}{N_{n+1}^{\text{eq}}}\right) = \frac{N_L}{N_L^{\text{eq}}} - \frac{N_{H+1}}{N_{H+1}^{\text{eq}}},\tag{15}$$

 $<sup>^{4}</sup>$ This approximation was originally made for dilute systems[17], where collisions between relatively rare larger clusters are rather rare. This will prove to be a rather poor assumption for the nucleation of cubes, as we will see in the next Section.

where we used the telescoping quality of the last sum. Now using the assumptions, we notice that  $N_L/N_L^{\text{eq}} \rightarrow 1$ and  $N_{H+1}/N_{H+1}^{\text{eq}} \rightarrow 0$ , simplifying Eq. 15 to

$$R = \left(\sum_{n=L}^{H} \frac{1}{k_{+,n} N_n^{\text{eq}}}\right)^{-1}.$$
 (16)

Now we use that  $N_n^{\text{eq}} = N_1 \exp[-\beta \Delta G(n)]$  as derived in Ref. [29], and make a few more approximations to calculate the sum. First, the sum is dominated by terms with  $n \approx n^*$ , as  $N_n^{\text{eq}}$  is smallest there. Second, we then Taylor expand  $\Delta G$  to second order around  $n = n^*$ . Third, we can approximate  $k_{+,n} \approx k_{+,n^*}$ . Lastly, we turn the sum into a continuous integral and let the lower and upper bounds go to  $-\infty$  and  $\infty$  respectively. We can then calculate the nucleation rate. First we apply all but the last approximation:

$$R \approx \left(\sum_{n=L}^{H} \frac{1}{k_{+,n^*} N_1 \exp[-\beta \left(\Delta G(n^*) + \frac{1}{2} \Delta G''(n^*) n^2\right)]}\right)^{-1}$$
$$= N_1 k_{+,n^*} e^{-\beta \Delta G(n^*)} \left(\sum_{n=L}^{H} \frac{1}{\exp[-\beta \frac{1}{2} \Delta G''(n^*) n^2]}\right)^{-1},$$

Then, turning the sum into an integral from  $-\infty$  to  $\infty$ , and using that  $\Delta G''(n^*) < 0$ , we recognize the Gaussian integral. This yields

$$R \approx N_1 k_{+,n^*} e^{-\beta \Delta G(n^*)} \left( \int_{-\infty}^{\infty} e^{-\beta \frac{1}{2} |\Delta G''(n^*)| n^2} \right)^{-1} = N_1 k_{+,n^*} \sqrt{\frac{\beta |\Delta G''(n^*)|}{2\pi}} e^{-\beta \Delta G(n^*)},$$
(17)

where the factor  $Z = \sqrt{\frac{\beta |\Delta G''(n^*)|}{2\pi}}$  is known as the Zeldovitch factor [1]. We can also write Eq. 17 as

$$R = \kappa \mathrm{e}^{-\beta \Delta G^*},\tag{18}$$

where  $\kappa = N_1 k_{+,n^*} Z$  is the *kinetic pre-factor*, and  $\Delta G^* = \Delta G(n^*)$  is shorthand for the height of the freeenergy barrier. Because of the exponential dependence of this nucleation rate on the barrier height, we know a great deal about the nucleation rate if we can determine the barrier height. This is what will do using umbrella sampling.

### 6.3 Umbrella Sampling

We will be calculating the free-energy barrier using the following relation (for a derivation see Ref. [1]):

$$\beta \Delta G(n) = \text{constant} - \ln(P(n)), \tag{19}$$

where P(n) is the probability of finding a cluster of size n. In order to sample clusters for larger n, we need to wait for a fluctuation large enough to overcome the free-energy barrier from classical nucleation theory. Because we want to study nucleation rates close to the freezing density i.e. with low supersaturation, the barrier will be high and it will take a long time before a fluctuation creates a cluster larger than the critical cluster size, above which crystallization of the entire system will occur. With current computation power it is effectively impossible to simply set up the simulation and wait long enough for large clusters to appear. One way to combat this is by using *umbrella sampling* or *multistage sampling*, introduced by Torrie and Valleau in 1974 [28].

Following Ref. [5], the basic idea is that we put a weight function  $W(\mathbf{r}^N)$  on top of the normal interaction potential, in order to bias the system towards a particular region in phase space that we are interested in. In this case, that is configurations with a certain cluster size. That is, we will accept moves with a probability proportional to

$$\pi(\mathbf{r}^N) = \exp[-\beta U(\mathbf{r}^N) + W(\mathbf{r}^N)].$$
(20)

In order to sample the system at various cluster sizes, we will use the weight function introduced by ten Wolde et al. [30]

$$W(\boldsymbol{r}^{N}) = \frac{\lambda}{2} \left( N(\boldsymbol{r}^{N}) - N_{\text{target}} \right)^{2}, \qquad (21)$$

where  $N(\mathbf{r}^N)$  is the size of the largest cluster of configuration  $\mathbf{r}^N$ , and  $N_{\text{target}}$  will be the *target cluster size*. The idea of this harmonic potential around  $N_{\text{target}}$  is that we allow the cluster size to fluctuate but stay near the target. The value of the *coupling parameter*  $\lambda$  determines how much we allow the cluster size to fluctuate. A higher coupling parameter gives a narrower distribution and vice versa. This will all become more clear in Section 7.2.

Because adding a biasing potential distorts the behaviour of the system, in order to get the expectation value of a measurable A from the actual system, we have to 'unbias' the measured results. This can be done relatively simply, as per the following calculation done in Ref. [5].

$$\langle A \rangle = \frac{\int d\mathbf{r}^N A(\mathbf{r}^N) \exp[-\beta U(\mathbf{r}^N)]}{\int d\mathbf{r}^N \exp[-\beta U(\mathbf{r}^N)]}$$
(22)

$$= \frac{\int d\boldsymbol{r}^{N} A(\boldsymbol{r}^{N}) \exp[-W(\boldsymbol{r}^{N})](\boldsymbol{r}^{N}) \exp[-\beta U(\boldsymbol{r}^{N}) + W(\boldsymbol{r}^{N})]}{\int d\boldsymbol{r}^{N} \exp[-W(\boldsymbol{r}^{N})] \exp[-\beta U(\boldsymbol{r}^{N}) + W(\boldsymbol{r}^{N})]}$$
(23)

$$= \frac{\int d\mathbf{r}^{N} \operatorname{exp}[-W(\mathbf{r}^{N})] \operatorname{exp}[-\beta U(\mathbf{r}^{N}) + W(\mathbf{r}^{N})]}{\int d\mathbf{r}^{N} \operatorname{exp}[-\beta U(\mathbf{r}^{N}) + W(\mathbf{r}^{N})]}$$
(24)

$$= \frac{\int d\boldsymbol{r}^{N} \exp[-W(\boldsymbol{r}^{N})] \exp[-\beta U(\boldsymbol{r}^{N}) + W(\boldsymbol{r}^{N})]}{\int d\boldsymbol{r}^{N} \exp[-\beta U(\boldsymbol{r}^{N}) + W(\boldsymbol{r}^{N})]}$$
(24)

$$=\frac{\langle A\exp[-W]\rangle_{\pi}}{\langle \exp[-W]\rangle_{\pi}},\tag{25}$$

where  $\langle \cdot \rangle_{\pi}$  denotes sampling in the system according to Equation 20.

# 7 Measurements

### 7.1 Creating a Metastable Liquid

In order to study nucleation we need a metastable liquid, that is, a liquid at a pressure where the free energy would be lower in the crystal phase. Because we do not want to investigate finite-size effects, we will be studying a relatively large system of N = 8000 cubes.

The first step to creating a metastable liquid is creating a good liquid. We make this by starting the system out on a simple cubic lattice at a density of  $\rho\sigma^3 = 0.1$ , at a low pressure of  $\beta p\sigma^3 = 1$ . The crystal immediately melts and after ten thousand Monte Carlo cycles the system is sufficiently disordered, and we start to 'crush' the system by setting a very high pressure of  $\beta p\sigma^3 = 10000$ . This effectively makes the system only accept volume moves which shrink the system, hence we call this step 'crushing.' By driving the density up as fast as possible, we try to retain the disordered liquid structure for the highest densities possible. From Ref. [24] we know that the coexistence density of a liquid with a crystal in this system is at  $\rho\sigma^3 = 0.45$ , so we investigate this density.

The second step is to check that we have not introduced any unphysical order in the system by subjecting it to an extreme pressure, so we take the system at density  $\rho\sigma^3 = 0.45$  and keep it at this density (i.e. by turning the system into an *NVT* ensemble starting from this configuration) for a million Monte Carlo cycles. We observed no crystal formation as expected.

The third and final step is to now equilibrate the system at varying pressures. Smallenburg et al. found that the coexistence pressure is at  $\beta p^* \sigma^3 = 6.16$  [24]. Therefore, we made systems at pressures  $\beta p \sigma^3 = 6.17, 6.18, 6.19, 6.2, 6.25, 6.3$ , and 6.4. We equilibrated these systems by letting them run at the desired pressure (i.e. now we turn the system back into an NpT ensemble) for five hundred thousand Monte Carlo cycles. The last step of each of these runs is now a metastable liquid at the desired pressure.

An important matter that we need to point out is that in the process of 'crushing' the system to high density, we found that translational order was picked up earlier than orientational order at the same order cutoff of  $d_{\rm cut} = 0.6$ . This is probably because as discussed in Section 5.2.1, the orientational order in the liquid phase is slightly lower, and so we could set the cutoff for crystallinity according to orientational order lower than for translational order. In any case, we decided to continue investigating only translational order as a first start. That is, we will only look at crystallinity according to translational order. The procedure is, however, exactly the same for orientational order.

#### 7.2 Free-Energy Barriers

In this Section we discuss the free-energy barriers found for cubes, using the umbrella sampling method described in Section 6.3. First we explain the step-by-step process of creating the free-energy barriers in Section 7.2.1 and then we go over all our results we got for different parameters in Section 7.2.2. The shape of the clusters that formed were not as we expected more or less spherical and we will go into detail on that issue in Section 7.2.3. Due to time constraints we have only studied crystalline cluster formation of cubes with respect to translational order.

#### 7.2.1 From Cluster Sizes to the Free-Energy Barrier

We start from a metastable liquid discussed in Section 7.1, at pressure  $\beta p \sigma^3 = 6.17$ , which is slightly above the coexistence pressure between the liquid and crystal phase for cubes which is at  $\beta p^* \sigma^3 = 6.16$  [24]. We record the largest cluster size (LCS) every 50 Monte Carlo cycles and obtain the distribution found in Figure 18. We see that it is very rare that a cluster larger than 20 cubes forms, so we start the first step of umbrella sampling with a target of  $N_{\text{target}} = 30$ . As was discussed in Section 5.2.1, we chose the order cutoff  $d_{\text{cut}} = 0.6$ . After some experimentation, we chose a coupling parameter of  $\lambda = 0.005$ . Now we let the system



Figure 18: A log plot of the distribution of largest cluster sizes of a simulation at pressure  $\beta p \sigma^3 = 6.17$ .



run for a million Monte Carlo cycles and record the size of the largest cluster every 50 cycles. The resulting distribution and the piece of the barrier obtained from it using Equation 19 can be seen in Figure 19.

Figure 19: The data obtained from the first 'umbrella step' with  $\beta p \sigma^3 = 6.17$ ,  $\lambda = 0.005$ ,  $d_{\rm cut} = 0.6$ . The target cluster size  $N_{\rm target} = 30$  has been marked with a dashed grey line. (a) The distribution of largest cluster sizes. (b) The piece of the free-energy barrier obtained from the distribution in (a).

As we can see from Figure 19a, the LCS distribution is slightly skewed because we cannot have clusters smaller than 1, and it becomes exceedingly likely to find (many) other clusters which are larger. Because of this, the left side of the free-energy barrier seen in Figure 19b goes up. As a more pedagogical example, see Figure 20 for the same process but at target  $N_{\text{target}} = 90$ . Here we see a much nicer Gaussian distribution of cluster sizes. Note that in both cases, the distribution is clearly peaked *left* of the target. This is because even though we impose a biasing potential to keep the LCS around a certain  $N_{\text{target}}$ , the system itself is biased towards smaller cluster sizes, i.e. it will more often than not accept a move which shrinks the cluster. This can be interpreted as being 'left' of the free-energy barrier from CNT, or in other words, it is free-energetically favourable to shrink the cluster.



Figure 20: The data obtained from a later 'umbrella step' with  $\beta p \sigma^3 = 6.17$ ,  $\lambda = 0.005$ ,  $d_{\rm cut} = 0.6$ . The target cluster size  $N_{\rm target} = 90$  has been marked with a dashed grey line. (a) The distribution of largest cluster sizes. (b) The piece of the free-energy barrier obtained from the distribution in (a).

From here the process is clear. We obtain a LCS distribution around  $N_{\text{target}}$ , and after some number of Monte Carlo cycles<sup>5</sup> the system is in equilibrium (with respect to the biasing potential). We then start the second 'umbrella step,' a new simulation that starts with a configuration from the previous step's equilibrium, and with a new  $N_{\text{target}} = 50$ . When this system is equilibrated we can start the third 'umbrella step' with  $N_{\text{target}} = 70$  et cetera. We continue until either we find the top of the barrier, or the target cluster size becomes too large with respect to the system. For this combination of parameters ( $\beta p \sigma^3 = 6.17$ ,  $\lambda = 0.005$ ,  $d_{\text{cut}} = 0.6$ ) the latter was the case, and we stopped at  $N_{\text{target}} = 800$ , which is 10% of the system size. We will discuss problems that arise from such relatively large cluster sizes in the next Section. In any case, from each step we obtain the LCS distribution and find the corresponding piece of the free-energy barrier. All distributions, as well as all pieces of the barrier are shown in Figure 21. Note that some distributions are not like the others: we see two clear peaks in the LCS distribution and some of the slopes of the free-energy barrier do not line up with their neighbour's slope. This is due to bad statistics as the cluster can sometimes get 'stuck' in certain configurations. This derails the correct building of the free-energy barrier, so care must be taken that we obtained good statistics. Also note that at the edge of each distribution, we have poor statistics, which is reflected in the calculated free-energy barrier pieces as wild fluctuations at the edges.

In any case, we see that the pieces of the free-energy barrier do not line up vertically as well. However, because we have overlap between the different distributions, we can properly shift every piece of the barrier by a constant, which would be the constant from Eq. 19. If we do this, we have constructed the free-energy barrier, seen in Figure 22. We have colored different pieces of the barrier in the colours red, green, blue, and yellow to be able to differentiate between neighbouring steps.



Figure 21: (a) The largest cluster size distributions for every target cluster size. (b) The unbiased pieces of the free-energy barriers. Note a few distributions are not like the others: we see two sharp peaks in the cluster size distribution, and in the pieces of the free-energy barrier we see that the slope of some neighbouring pieces do not line up either. This is due to bad statistics.

We see that we have not found the top of the barrier for this combination of parameters. A possible reason for this could be that the supersaturation is too low (i.e. we need higher pressure), so as a result the size of the critical cluster is simply too large to explore with N = 8000 cubes. For this reason, we will now try higher pressures and see what the effect is of changing the coupling parameters and order cutoffs, and discuss our findings.

 $<sup>{}^{5}</sup>$ The number varies but if we waited a hundred thousand cycles we had no problems in the next step. If we do not wait long enough for many 'umbrella steps' however, we can get into a situation where the target cluster size is so much larger than the actual cluster size that the system gets 'stuck' in a very unstable cluster, causing very poor statistics.



Figure 22: The free-energy barrier obtained by stitching together every piece shown in Fig. 21. For completeness, the parameters for this barrier were  $\beta p \sigma^3 = 6.17$ ,  $\lambda = 0.005$ ,  $d_{\rm cut} = 0.6$ .

#### 7.2.2 Results - Barriers

We now discuss the free-energy barriers we found for various combinations of pressures, coupling parameters, and order cutoffs. As we saw in Section 7.2.1, we did not find the top of the barrier for  $\beta p \sigma^3 = 6.17$ . We first show the barriers we were able to calculate, and then discuss problems we ran into. We were not able to investigate all problems fully, due to time constraints. In order to get good statistics on a single umbrella step, we need to run for about two million Monte Carlo cycles, which takes more than five days. We are able to properly start the next umbrella step within about eight hours of the previous step, but even so we need a lot of computing time, considering we needed almost 40 umbrella steps to obtain Figure 22. For this reason and the problems we will discuss momentarily, we have only looked at crystallinity with respect to translational order for cubes.

We found a barrier of  $\Delta G^* \approx 30k_BT$  with critical cluster size  $n^* \approx 500$  for pressure  $\beta p\sigma^3 = 6.25$ ,  $\lambda = 0.005$  and order cutoff  $d_{\rm cut} = 0.7$ , see Figure 23. As we can see the total barrier is relatively smooth, indicating that we have relatively good statistics.



Figure 23: The free-energy barrier associated with  $\beta p \sigma^3 = 6.25$ ,  $\lambda = 0.005$ ,  $d_{\rm cut} = 0.7$ .

Next we look at the free-energy barrier found from simulations with some lower pressures  $\beta p \sigma^3 = 6.19, 6.20, d_{cut} = 0.7$ , and examine the effect of the coupling parameter  $\lambda$  using  $\lambda = 0.005$  and  $\lambda = 0.01$ . The results can be seen in Figure 24. Note that the free-energy barrier should not change when we change  $\lambda$ , as it is a parameter of umbrella sampling, which we account for. Also important to point out is that for the  $\lambda = 0.01$  run, we used the ending configuration of the  $\lambda = 0.005$  run. This means the system should be well equilibrated, but the configurations could be correlated. For the  $\beta p \sigma^3 = 6.19$  case, we find a free-energy barrier of



Figure 24: The free-energy barriers obtained with pressures  $\beta p \sigma^3 = 6.19$  and  $\beta p \sigma^3 = 6.20$ , order cutoff  $d_{\text{cut}} = 0.7$ , and a comparison between coupling parameters  $\lambda = 0.005$  and  $\lambda = 0.01$ .

 $\Delta G \approx 42k_BT$  for a cluster size  $n \approx 450$  cubes in the  $\lambda = 0.005$  case (Fig. 24a), but a barrier of  $\Delta G \approx 36k_BT$  for the same cluster size in the  $\lambda = 0.01$  case (Fig. 24b). We should be wary, however, as we did not sample for larger cluster sizes, and we cannot yet truly see the free-energy cost go down. Furthermore, in Figure 24a we see evidence of poor statistics, because some of the free-energy barrier pieces do not go smoothly from one to the next. We can have effectively the same discussion in the  $\beta p \sigma^3 = 6.20$  case (Figures 24c and 24d). Here we find free-energy barriers of  $\Delta G \approx 47k_BT$  for a cluster size of 500 cubes in the  $\lambda = 0.005$  case (Fig. 24c), but  $\Delta G \approx 40k_BT$  at the same cluster size in the  $\lambda = 0.01$  case (Fig. 24d). Because we cannot see the barrier go down yet, we cannot conclusively determine the critical cluster size, but we do see that the barriers differ by many  $k_BT$ .

Now we discuss some problems which emerged in building the barrier. First of all, we need to address the cluster size. An interesting observation of these systems is that typically, the clusters that form are not quite spherical. Instead, a cluster can form long branches of crystallinity. We will go into more detail of this phenomenon in Section 7.2.3. A consequence of this is that when  $N_{\text{target}}$  is larger than about 500 cubes it becomes likely that the system will form a *system-spanning* cluster. That is, one part of the cluster will be connected via periodic boundary connections to the other side of the cluster, effectively forming a sort of 'tube' of crystallinity, rather than a cluster. An example can be found in Figure 25, where a system-spanning cluster has formed at a target  $N_{\text{target}} = 580$ . This is a finite-size effect we do not take into account, but which will impact our findings. The only way around this is to simulate even larger systems, therefore this is problematic. For this reason we do not consider targets much larger than 600.



Figure 25: A system-spanning cluster has formed at a target cluster size of  $N_{\text{target}} = 580$  with parameters  $\beta p \sigma^3 = 6.25$ ,  $\lambda = 0.005$ ,  $d_{\text{cut}} = 0.6$ .

We also want to note that our initial order cutoff of  $d_{\rm cut} = 0.6$  which we decided on in Section 5.2.1 did not give us good statistics, nor did we find the top of the free-energy barrier. See Figure 26, where we investigated  $\beta p \sigma^3 = 6.20$  and  $\beta p \sigma^3 = 6.25$  for  $\lambda = 0.005$  and  $d_{\rm cut} = 0.6$ . We find that for example in Fig. 26a the free-energy barrier grows almost linearly for a large range of cluster sizes, which is not what we expect. Moreover, in both Figure 26a and 26b we see after careful inspection that the pieces of the barrier do not line up well. It is likely that  $d_{\rm cut} = 0.6$  is simply not restrictive enough, meaning that we are looking at local fluid order and not crystal order.



Figure 26: The incomplete free-energy barriers obtained with pressures  $\beta p \sigma^3 = 6.20$  and  $\beta p \sigma^3 = 6.25$ , coupling parameter  $\lambda = 0.005$ , and order cutoff  $d_{\text{cut}} = 0.6$ .

As a sanity check we also look at higher pressures of  $\beta p \sigma^3 = 6,30$  and  $\beta p \sigma^3 = 6.40$ , which are relatively far above the coexistence pressure of  $\beta p^* \sigma^3 = 6.16$ . See Figure 27. At high pressure we expect to see either a very low barrier, or no barrier at all. In Fig. 27a we see that the free-energy barrier has a maximum at about a cluster size of about 200. Note however that there is clear evidence of bad statistics, as not only do we some pieces not lining up with neighbouring piece, but also we see that the free-energy barrier flattens out which is not what we expect. Unfortunately due to time constraints we could not investigate why the barrier flattens out. In Fig. 27b, we see a very different barrier, in fact it is not much of a barrier at all. Again, we have bad statistics as the pieces do not line up, but more importantly, we see that even the first umbrella step results in a piece of the barrier with a downward slope. It seems like effectively there is no barrier, which is reminiscent of spinodal decomposition.



Figure 27: The free-energy barrier obtained at a higher pressures of  $\beta p \sigma^3 = 6.30$ , 6.40. Note that most pieces do not line up due to bad statistics.

#### 7.2.3 Results - Cluster Shape

We now discuss an interesting feature of cube nucleation that we discovered. As was already mentioned, the clusters we observed are not well approximated by spheres. In fact, they more often than not form branches, or are generally long. This was unexpected, as clusters for hard spheres do not show this behaviour, see Figure 28a taken from Ref. [8]. We compare this to an example of what can happen in the case of hard cubes, seen in Figure 28b. Here we see a small cluster of only 105 cubes which spans about two thirds of the simulation box. This cluster can be better described as 'connected clumps of crystallinity' than as a spherical cluster. Also note that Figure 28b, we see a lot of crystallinity detected in the fluid phase, indicating that the order cutoff of  $d_{\rm cut} = 0.6$  used here, which was determined in Section 5.2.1 is too low.



Figure 28: A comparison between clusters. (a) A more or less spherical cluster of hard spheres, taken from Ref. [8]. (b) A long cluster of 105 cubes from a simulation with pressure  $\beta p \sigma^3 = 6.17$  and  $d_{\text{cut}} = 0.6$ .

Another side effect of the 'tendril-like' structure of the cluster is that it hampers our ability to obtain decent statistics by slowing down the simulation. Often, moves are attempted which break off a large part of the cluster, see Figure 29 for an illustration. These steps will not be accepted due to the high energy cost of the umbrella potential, so it means a lot of computation time is spent on creating configurations which will be rejected.



Figure 29: A large cluster from a simulation with a target cluster size of  $N_{\text{target}} = 700$  with parameters  $\beta p \sigma^3 = 6.17$ ,  $\lambda = 0.005$ ,  $d_{\text{cut}} = 0.6$ . (a) A cluster of 722 cubes. (b) A few steps later, a move is attempted which breaks the cluster in two, the largest of which has only 389 cubes.

Part IV Conclusion & Outlook In this thesis we used Monte Carlo simulations to investigate the nucleation of hard (slanted) cubes. In Part I, we set up the model and examined the phase behaviour by looking at the equations of state for a variety of slant angles. We found our equations of state consistent with previous work done with the same model. We observed a low density liquid and a high density crystalline phase, and importantly, observed hysteresis between the two phases. This hysteresis is typical of a first-order phase transition and indicates the 'resistance' to phase change. Interestingly, we saw that for smaller slant angles, the hysteresis between the two phases was larger. This could be an indication that the surface tension between the crystal and liquid phases are larger.

In Part II, we explored the structure of both the liquid and crystal phases. We determined the relevant length scales for each phase using the radial distribution function, and used this information to quantify crystalline order. We did this for both translational and orientational order, using the *Steinhardt* order parameters [25]. We also discussed and resolved a possible problem in the definition of orientational order in slanted cubes. The main result from this part was that we found that the order parameter was suitable for distinction between the liquid and crystalline phase for both translational and orientational order. Using the length scales we established, we could properly differentiate between fluid and crystalline environments.

In Part III we then applied this analysis to finally investigate nucleation. First we discussed classical nucleation theory and how nucleation rates can be determined from the free-energy barrier. In order to obtain the free-energy barrier, we need to get statistics on clusters of every size. To do this, we discussed and applied *umbrella sampling*. Using umbrella sampling we could force clusters to stay near a target size. We calculated some free-energy barriers, but it was at this point we faced some challenges inherent to the system of hard cubes. Interestingly, we found that unlike in systems of e.g. hard spheres, clusters of hard cubes do not form roughly spherical clusters. This had several consequences. One is that the often long shape of the cluster makes it likely for system-spanning clusters to form. This is a problem, because the only way around it is by simulating very large systems. A second effect is that often, large parts of a cluster in two, which will be rejected by the umbrella biasing potential. Therefore we spend a lot of computational power on moves which we will not sample, therefore slowing down the simulation. These problems made it so that we only had time to investigate translational order in cubes.

The next few steps in researching this topic are clear. Not only can the free-energy barriers be studied more closely, especially those with poor statistics, but also can the same nucleation analysis be done with respect to orientational order. The resulting clusters can then be compared with the clusters obtained from translational ordering in this thesis. Particularly interesting would be to study the emergence of orientational order in clusters obtained from translational ordering and vice versa. This way we could answer the question of which type of order comes first: translational, or orientational. Furthermore, the same analysis can straightforwardly be applied to the case of slanted cubes, which, for smaller slant angles display more hysteresis. Studying the effects of slant angle is an especially promising way forward, because the increased hysteresis is an indication of higher surface tension, which would lead to more spherical clusters. As discussed, this would mitigate a lot of problems encountered in the study of nucleation of cubes.

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