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New techniques for simulating crystals

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ABSTRACT

Methods for simulating solid crystalline phases are generally not as straightforward as those for fluids. This work discusses the reason for this and reviews some recently developed Monte-Carlo techniques for simulating crystalline phases. The self-referential method for calculating crystal free energies is described first. This technique is particularly straightforward and it is expected to be very versatile. Next, a novel kind of Gibbs ensemble method adapted to treat crystalline solid – fluid coexistence is described. This technique requires free energy calculations of the crystalline phase as input, and of course these can be provided by the SR method.

1 Introduction

1.1 Background

The crystalline state is fundamental in nature, and molecular simulation is increasingly used to understand and predict the properties of matter. Yet, despite this, molecular simulation techniques for molecular crystals are in general not as satisfactory as those for fluids, and there is some debate about how confined crystals can be simulated correctly. This paper reviews some recent work that has made some progress in this area¹⁻⁴ and which aims to make simulation of crystals, especially confined crystals, easier.

Crystal phase diagrams are usually much more complex than those of the corresponding fluid phases. This complexity increases when one considers molecular crystals, compared to atomic (spherical) species, and is likely to increase further under confinement, such as within a slit-pore, due to the

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3 shifting of bulk transitions and the potential introduction of surface induced transitions. The precise
4 knowledge of a molecular crystal phase diagram can be of tremendous practical and economical
5 interest, for instance in the pharmaceutical industry, where the impact of crystal polymorph can be
6 almost as important as the choice of chemical compound on its possible prescription as a drug. And
7 the prediction of freezing in confined environments, e.g. within porous materials, can be useful for
8 many engineering processes that involve adsorption of fluids. Moreover, crystal phase diagrams can
9 be sensitive to the choice of molecular model⁵, and so crystal phase diagram prediction can be used as
10 another mechanism for fine-tuning molecular models. So it is important to be able to easily and
11 straightforwardly map the phase diagrams of both bulk and confined molecular crystals via molecular
12 simulation.
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27 Central to the problem of simulating crystals is calculation of free energy. It is even more important to
28 know the free energy for crystals than for fluids. This is not just because phase transitions involving
29 crystalline solids are often strongly first-order and associated with significant hysteresis – a particular
30 problem with simulations. It is also because we cannot impose or measure the bulk (i.e. experimental)
31 pressure when simulating confined crystals, unless an impractically large system is simulated that
32 includes the confined system – bulk system interface. Instead, it is essential that the chemical potential
33 of the confined crystal is known (imposed or measured), because this quantity is the same in the
34 confined and bulk systems at equilibrium. Unfortunately, we cannot impose the chemical potential on
35 simulated crystals by performing grand-canonical ensemble simulations. The reasons for this are
36 explained in detail in section 1.2 below. Instead, we should perform simulations that allow the crystal
37 to relax to an equilibrium state, and then seek to measure the chemical potential of the crystal. For
38 bulk crystals the isothermal-isobaric (NPT) ensemble⁶ is an obvious choice, while for crystals
39 confined in uniform slit-pores, for example, simulations at constant interfacial tension ($N\sigma T$) are
40 appropriate (Figure 1 shows a sketch of this ensemble). For a pure system the chemical potential is
41 then simply the Gibbs free energy per particle. So for simulation studies of confined crystals
42 calculation of the Gibbs free energy is essential if conditions inside the pore are to be related to
43 experimental (or bulk) conditions, regardless of whether phase behaviour is of interest or not. In
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3 section 2 of this paper I summarize an approach for performing such free energy calculations, the self-
4 referential (SR) method, developed in recent years¹⁻³, which is significantly more straightforward than
5 other methods. Although the most recent version of this technique (which incorporates a kind of
6 thermodynamic integration) has so far only been applied to bulk crystals, it is expected that it can also
7 be applied unchanged to confined crystals.
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16 The Gibbs ensemble⁶⁻⁸ is a convenient and popular Monte-Carlo method for simulating phase
17 coexistence. Its main advantages are that coexisting states are generated spontaneously during a single
18 simulation (given reasonable initial conditions) and that relatively small systems can be simulated
19 because a phase interface is not required. Unfortunately, this method can fail if one or both of the
20 coexisting phases are either very dense or solid. For dense liquid phases the method can fail if the
21 acceptance rate for particle transfers between phases becomes too low, although specialised algorithms
22 should improve transfer acceptance rates for certain cases⁹. However, the method fails when one or
23 more of the phases are crystalline for a more fundamental reason, which is again discussed in section
24 1.2. However, it is possible to apply the Gibbs simulation technique to crystalline solid phases in an
25 indirect way, and Section 3 summarizes work that shows how this can be achieved. This technique⁴
26 relies on generation of an accurate canonical Helmholtz free-energy model for the crystal phase. In
27 turn, this free energy model relies on calculation of the Gibbs free energy for a trial crystalline state
28 not too far from coexistence, which in turn can be calculated via the SR approach just discussed. So
29 we see, once again, the importance of free energy calculations for simulations of crystalline solids.
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49 This work summarizes both the SR method (section 2) and the Gibbs ensemble method applied to
50 solid-fluid coexistence (section 3). But first in section 1.2 we discuss the reason why crystals are not as
51 easy to simulate as fluids, namely because of conflict in symmetry requirements.
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1.2 *A conflict of symmetry requirements*

We know that for specified thermodynamic conditions (temperature and chemical potential or pressure) only one lattice site density corresponds to the equilibrium state. So, a simulated crystal must be able to adjust its lattice site density (provided it is not somehow initiated in the equilibrium state) in response to these external conditions. With grand-canonical simulations volume is fixed, so equilibrium is achieved by fluctuations in particle number in response to an applied chemical potential. However, when simulating a space-filling crystal with periodic boundary conditions this kind of fluctuation does not lead to a change in the lattice site density. Instead, it can lead only to changes in the number and kind of defects; it leads to the wrong kind of fluctuation. So in principle, regardless of the how well particle number fluctuations are sampled, equilibrium simulations of crystals cannot be performed with the grand canonical ensemble and periodic boundaries. Of course, for a space filling crystal fluctuations in lattice spacing in different directions can be achieved at fixed volume by shortening one box length while simultaneously lengthening another or by adjusting vertex angles. However, in this case spacing in one direction is traded against another, and although the crystal might be able to relax somewhat, this will still not allow full relaxation to the equilibrium lattice site density which is fixed because the overall volume and number of lattice sites is fixed. One might argue that it might be possible to develop Monte-Carlo moves that allow an entire slice of unit cells to be added or removed from one side of the crystal simulation box, or to adapt Tilwani and Wu's¹⁰ re-tiling algorithm to 3-D crystals. But if this is achieved then in general this would not correspond to the grand canonical ensemble which requires molecule-by-molecule fluctuations rather than fluctuations in the number of unit cells. This problem is a matter of principle, and not concerned with clever insertion/deletion strategies.

Let us consider why this is the case. If instead the system was fluid, or even if it was a liquid crystal, i.e. if it did not possess crystalline translational symmetry in at least one direction, then the right kind of fluctuations could occur, even with periodic boundaries, in response to an applied chemical potential. So the fluid could adjust its average density perfectly in response to any change in chemical

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3 potential. Also, if the crystal simulation, somehow, did not employ periodic boundaries then, again,
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5 the correct kind of fluctuation could be simulated and the crystal could adjust its average density
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7 perfectly in response to any change in chemical potential. But when we have both crystalline
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9 symmetry and periodic boundaries simultaneously we encounter this problem. So the problem occurs
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11 because of a conflict in symmetry requirements between crystalline translational symmetry and
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13 periodic boundary conditions.
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18 Note that this is not a finite-size effect, i.e. this problem is not automatically resolved by simulating a
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20 sufficiently large system, because no matter how large the system one cannot guarantee that it will be
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22 initiated with the correct lattice site density, and in general molecule-by-molecule fluctuations in the
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24 lattice site density cannot occur at fixed volume.
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29 The same problem would arise if one attempted a standard Gibbs simulation involving a crystalline
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31 solid phase. Once again, the crystalline phase must be able to adjust its average lattice site density so
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33 that the chemical potentials of the coexisting phases are equilibrated. Although the lattice spacing can
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35 adjust so that pressure is equilibrated, it cannot adjust in response to particle exchanges which are
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37 responsible for equilibrating chemical potential. Any particle exchanges that do occur must result in
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39 creation or annihilation of defects, which by themselves do not create any change in the average
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41 lattice spacing.
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47 Because of these problems it is standard practice to perform simulations of crystals with periodic
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49 boundary conditions using the isothermal-isobaric ensemble, or the equivalent ensemble for confined
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51 crystals where the interfacial tension (the negative of the average of the transverse component of the
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53 pressure tensor for a crystal confined within slit-pore for example) is fixed. Although the number of
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55 particles is fixed, the simulation cell volume can fluctuate with these simulations, and so the lattice
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57 site density can relax to its equilibrium value.
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3 Despite this, there are a rapidly growing number of examples¹¹⁻³³ in the literature where the grand
4 canonical ensemble is used to simulate space-filling crystalline solids, particularly confined crystals.
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6 All this work should be considered carefully, because in every case these are not equilibrium
7 simulations and each result is subject to systematic error. So the precise location of fluid-crystal phase
8 transitions for bulk and confined systems are in doubt. In particular, Gubbins and colleagues¹²⁻³³ have
9 performed many studies of bulk and confined crystals using the grand canonical ensemble together
10 with a kind of Landau free energy technique, which is essentially a non-Boltzmann or biased
11 sampling method. The aim in these studies is to measure the (grand) free energy difference between a
12 liquid and crystalline state. This is achieved by starting with one state (liquid or crystal) and traversing
13 a path, along an order parameter that measures the system's degree of crystalline order, to the other
14 state. The free energy difference is integrated along this path. The problem with this technique in this
15 case is that the crystal end point of this path does not correspond to an equilibrium crystal at the
16 specified chemical potential for the reasons given above, i.e. the volume is fixed in advance. If the
17 simulation cell volume is large and the process is initiated with a liquid state, then as the path towards
18 the crystal state is taken the system might adopt a lattice site density close to the equilibrium value.
19 But this is not guaranteed, and the difference between the final lattice site density and the actual
20 equilibrium lattice site density corresponding to the applied chemical potential will depend on the
21 initial choice of volume. Despite this problem, results obtained using this method are in broad
22 agreement with experiment, so it is likely that systematic are not large. Nevertheless, it is always
23 preferable to formulate simulation strategies that are in principle exact so that the only error is
24 statistical.
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51 The above arguments also apply to quasi 2-dimensional crystals that form on the inner surface of a
52 slit-pore where the pore width is fixed and fluid fills the middle of the pore. Once again, they key
53 issue is whether the crystal can adjust its lattice site density to reach equilibrium in response to an
54 applied chemical potential. If the pore width is fixed then the lattice site density is determined by the
55 area of the slit-pore, which is fixed in advance with a grand canonical simulation. So simulations of
56 crystals on the surface of slit-pores with fixed pore width using the grand canonical ensemble are also
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3 not equilibrium simulations, unless the correct pore area (or lattice site density) is known in advance.
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5 Once again, the work of Gubbins and colleagues¹²⁻³³ in this area must be viewed with caution because
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7 all their results will exhibit systematic errors that depend on the difference in the true equilibrium
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9 lattice site density corresponding to the applied chemical potential and the lattice site density that
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11 actually develops spontaneously in their simulations, which is influenced by the initial choice of pore
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13 area.
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15 16 17 18 **2 The self-referential method** 19

20 As explained above in the introduction, methods for calculating the free energy are important for
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22 crystals, particularly confined crystals for which the chemical potential must be calculated if the
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24 corresponding bulk or reservoir state is to be determined. Several methods³⁴⁻⁴² have been developed
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26 for calculating the canonical Helmholtz free energy of crystals, which are also sufficient for
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28 calculating the chemical potential provided the pressure is known or can be calculated (either the bulk
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30 pressure or the interfacial tension for a confined crystal). Probably the most popular such free energy
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32 methods are those based on an Einstein crystal reference state^{34,37,38,40-42}, for which comprehensive
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34 texts^{5,6,43,44} have been published.
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40 However, the Einstein crystal route is not a very convenient method for confined crystals because the
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42 pore walls need to be 'integrated away' to make a path from the confined crystal to the Einstein
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44 crystal (the Einstein crystal is a non-interacting state, and so there cannot be any pore walls in this
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46 state). Additional simulations are needed to achieve this, and it is not clear that this is a
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48 straightforward procedure. For example, the precise path chosen might depend on the molecule – wall
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50 interaction type, i.e. hard or continuous potentials, and on the possible existence of any surface
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52 induced phase transitions. The aim of work that led to the self-referential method³ (at least, the
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54 version of the self-referential method described here) was to develop a method that is able to treat
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56 bulk and confined crystals on an equal footing. That is, to develop a method that did not require the
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58 pore walls to be integrated away. So far, the version of the self-referential method described in the
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60 next section has been applied successfully only to bulk crystals¹⁻³. Work aimed at applying it to

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3 confined crystals is ongoing, although it should be noted that the original version⁴⁵ of the self-
4 referential method was applied in the context of hard rods on a line, which can be considered an
5 extreme case of confinement for hard spheres in a cylindrical pore.
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11 The self-referential (SR) method calculates the free energy difference between two crystalline solid
12 systems that are identical except for their size (see Figure 2). If the free energy corresponding to the
13 ensemble used is extensive, and if the large system is twice the size of the small system, then this free
14 energy difference is also the free energy of the small system. So the small system is a kind of
15 reference state, hence the name of this method. In early work Barnes and Kofke⁴⁵ developed and
16 applied the self-referential method to 1-D hard-rods on a line using the canonical ensemble and a
17 technique based on sampling vibrational modes. They obtained good agreement with exact grand
18 canonical results indicating that their system was sufficiently large. They coined the phrase ‘self-
19 referential’ for this general idea. Later, this idea was re-invented³ in the context of 3-dimensional
20 crystals and applied to hard sphere and Lennard-Jones crystals using the isothermal-isobaric ensemble
21 and a kind of ‘parameter hopping’ Monte-Carlo technique. Once again, comparison with reference
22 literature results showed that the self-referential method was feasible and correct. However, this early
23 version of the method is not efficient. The reason for this is that the free energy difference between
24 the large and small system is actually relatively large, and so many parameter hops, typically several
25 thousand – each requiring a single simulation, are needed to traverse the path between the large and
26 small systems. Note that this particular technique is not an essential part of the SR method. Recent
27 work^{1,2} has shown how the efficiency of the SR method can be improved dramatically by
28 implementing a kind of thermodynamic integration (SR-TI), to the point where the SR method can
29 now be considered useful, and it is this version of the method that is summarized next. The latest
30 version¹ also employs the canonical ensemble, which is considered slightly more convenient for bulk
31 crystals, and has been extended and applied to crystals composed of rigid linear molecules
32 (specifically homonuclear hard and Lennard-Jones dumbbells), and validated once more against
33 reference literature data. This latest work also stated (but did not prove) that the method could be
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3 applied to arbitrary space-filling crystals, and provided a general formula for the reduced canonical
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5 Helmholtz free energy difference per particle that is also presented in the next section.
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8 9 10 **2.1 Theory**

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12 This section briefly summarizes the derivation of the main equations of the SR-TI technique^{1,2}. As
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14 described above, it is more convenient to formulate the method using the canonical ensemble and this
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16 is how it will be described next, although a discussion of how to use it with the isothermal-isobaric
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18 ensemble will also be given later. This technique uses two steps, ‘replication’ and ‘relaxation’, to
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20 compute the free energy difference between the large and small systems. Starting with the small
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22 system, the replication step computes the free energy difference between the small system and a
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24 double-size system that is constrained so that it is self-similar, i.e. the two halves of the system are
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26 almost identical in terms of particle degrees of freedom, except of course that the replicated half is
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28 translated with respect to the original half (see Figure 2). Note that there are always periodic boundary
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30 conditions; the small and large systems are *not* isolated. The relaxation step computes the free energy
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32 difference between this self-similar double-size system and the normal, fully-relaxed double-size
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34 system. Adding these two steps together gives the total free energy difference between the small
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36 system and the double-size system, which is the (negative of) the free energy difference we seek.
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42 43 **2.1.1 Replication**

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45 The replication step can be calculated analytically. To see this we first have to define the partition
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47 functions for the small, constrained double-size, and relaxed double-size systems. If we focus on
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49 particles with only positional coordinates initially for convenience, a canonical ensemble partition
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51 function for a system of N such molecules is in general given by
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$$55
56 \Phi = \frac{\Lambda_t^{3N}}{N!} \int_V d\mathbf{r}^N e^{-\beta H(\mathbf{r}^N, V)} \quad (1)
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3 where r_i is the position of particle i , $d\mathbf{r}^N$ indicates the volume element corresponding to the $3N$
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6 positional coordinates of all the particles, $\Lambda_i = \sqrt{2\pi mk_B T / h^2}$ is the translational contribution
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8 obtained by integrating over momenta, H is the configurational contribution to the Hamiltonian and
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10 $\beta^{-1} = k_B T$ (k_B is Boltzmann's constant and T is temperature). Note that the momentum contribution
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12 to the free energy is not important because it is the same for all phases, so it is dropped from here on.
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14 Only the configuration contribution is important in the context of phase behaviour. More complex
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16 particles with other degrees of freedom will be considered later.
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22 Of course, we know that identical microstates must only be counted once, and this issue needs careful
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24 consideration^{5,46,47}. The factor of $N!$ in (1) arises because normally there are no restrictions on the
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26 positions of molecules relative to each other. So each microstate has $N!$ permutations, obtained by
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28 repeatedly swapping labels on pairs of molecules. However, if with a simulated crystal we restrict the
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30 positions of each molecule relative to each other, then only N such permutations are possible. These N
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32 permutations are obtained by translating the entire system (remember we have periodic boundary
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34 conditions), with fixed relative molecular positions, so that molecule 1 visits the position of each of
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36 the other lattice sites. So, provided our simulations only sample one permutation of relative molecular
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38 positions (this constraint is indicated by the symbol V'), the partition function can be written as
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40 (without the momentum contributions now)
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$$\Phi = \frac{1}{N} \int_{V'} d\mathbf{r}^N e^{-\beta H(\mathbf{r}^N, V)} \quad (2)$$

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51 Finally, by clamping molecule 1 at a particular position we can write this as
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$$\Phi = \frac{V}{N} \int_{V'} d\mathbf{r}^{N-1} e^{-\beta H(\mathbf{r}^N, V)} \quad (3)$$

Our aim, then, is to calculate the sum of the replication and relaxation free energy differences which are

$$\beta\Delta(F) = \Delta(\beta F_{rep}) + \Delta(\beta F_{rel}) = -\ln\left(\frac{\Phi_{\alpha_1}}{\Phi_s}\right) - \ln\left(\frac{\Phi_d}{\Phi_{\alpha_1}}\right) \quad (4)$$

where the subscripts stand for the single-size system (s), the highly constrained self-similar double-size system (α_1), and the normal double-size system (d). This subscript notation is used throughout. Self-similarity of the double-size system is enforced via a constraint term in the configurational part of the Hamiltonian

$$H_{\alpha}(r^{N_d}, V_d) = H_0(r^{N_d}, V_d) + \sum_{i=1}^{N_s} \phi(r_i - \alpha) \quad (5)$$

where $r_i = |\mathbf{r}_{i+N_s} - \mathbf{L}_x - \mathbf{r}_i|$, H_0 is the Hamiltonian for an unconstrained system of particles, and where the constraint function is the infinite step-function,

$$\phi(r) = \begin{cases} \infty & ; \quad r > 0 \\ 0 & ; \quad r \leq 0 \end{cases} \quad (6)$$

Note that the nature of the interaction between the particles has not been specified. It could be defined by a pair potential, or even a higher order multi-body potential. At present the only requirement is that the particles only have positional degrees of freedom, and so any pair potential is necessarily spherically symmetric. In equation (5) N_s is the number of particles in the small system, \mathbf{L}_x is the ‘replication vector’ equal to half the double-size simulation box side (assumed to be in the x-direction here) and α controls the degree of self-similarity, or equivalently the degree of relaxation. That is, when α is very small the double-size system is almost perfectly self-similar and when α is very large

the double-size system is perfectly relaxed. Indeed, when $\alpha = \alpha_1$ the self-similarity constraint is so severe that we can perform the integrals over the replicated particles degrees of freedom immediately because the Hamiltonian is essentially constant over the phase space accessible to each replicated particle. We obtain a contribution $V_{\alpha_1} = 4\pi\alpha_1^3/3$ per replicated particle, i.e. the phase space volume available to each replicated particle. At the same time, because the double-size system is self-similar, we can write $H_{\alpha_1}(r^{N_d}, V_d) \cong 2H_0(r^{N_s}, V_s)$, and so the replication term is

$$\Delta(\beta F_{rep}) \cong -\ln \left(\frac{\frac{V_{\alpha_1}^{N_s} V_d}{N_d} \int_{V'_s} d\mathbf{r}^{N_s-1} \exp(-2\beta_{\alpha_1} H_0(N_s, V_s))}{\frac{V_s}{N_s} \int_{V'_s} d\mathbf{r}^{N_s-1} \exp(-\beta_s H_0(N_s, V_s))} \right) \quad (7)$$

Notice that the temperature of the double-size system when $\alpha = \alpha_1$, denoted β_{α_1} , is allowed to be different to the temperature of the system we are interested in, β_s . By setting $2\beta_{\alpha_1} = \beta_s$ we obtain

$$\Delta(\beta F_{rep}) \cong -N_s \ln(V_{\alpha_1}) \quad (8)$$

which is exact in the limit $\alpha_1 \rightarrow 0$.

2.1.2 Relaxation

The relaxation free energy difference is conveniently calculated using a kind of thermodynamic integration

$$\Delta(\beta F_{rel}) = \int_{\alpha_1}^{\alpha_m} d\alpha \frac{d(\beta_\alpha F_\alpha)}{d\alpha} \quad (9)$$

where $\beta_\alpha F_\alpha = -\ln \Phi_\alpha$ and α_m is so large that it has no effect on the system. The differential can be written as

$$\frac{d(\beta_\alpha F_\alpha)}{d\alpha} = -\frac{1}{\Phi_\alpha} \frac{d\Phi_\alpha}{d\alpha} \quad (10)$$

The partition function depends on α through both the temperature and the Hamiltonian as follows. As α increases the temperature must decrease so that $\beta_\alpha = \beta_s$ when $\alpha = \alpha_m$. Also, as α increases the self-similarity constraint relaxes until it no longer has any effect. By the chain rule we obtain

$$\frac{d(\beta_\alpha F_\alpha)}{d\alpha} = \left\langle \beta_\alpha \frac{\partial H_\alpha}{\partial \alpha} + H_\alpha \frac{\partial \beta_\alpha}{\partial \alpha} \right\rangle \quad (11)$$

where H_α is the Hamiltonian corresponding to Φ_α and hence F_α , and where the angle brackets denote an ensemble average. So we have two contributions to $\Delta(\beta F_{rel})$; one due to changes in temperature

$$\Delta(\beta F_T) = \int_{\beta_s/2}^{\beta_s} \langle H_\alpha \rangle d\beta_\alpha \quad (12)$$

and another due to changes in the self-similarity constraint,

$$\Delta(\beta F_\alpha) = \int_{\alpha_1}^{\alpha_m} d\alpha \left\langle \beta_\alpha \left(\frac{\partial H_\alpha}{\partial \alpha} \right) \right\rangle_\alpha \quad (13)$$

The first contribution, $\Delta(\beta F_T)$, can be evaluated using numerical quadrature. To calculate contribution (13) we must first differentiate the Hamiltonian with respect to α . This is not so straightforward, and rather than repeating the derivation in earlier work the result is simply stated

$$\Delta(\beta F_\alpha) = -4\pi N_s \int_{\alpha_1}^{\alpha_m} d\alpha g_\alpha(r = \alpha) \alpha^2 \quad (14)$$

Here, $g_\alpha(r)$ is the average ‘partner’ distribution function $g_\alpha(r) = N_s^{-1} \sum_i g_{\alpha i}(r_i = r)$, where $g_{\alpha i}(r_i)$ is the individual partner distribution function for the separation $r_i = |\mathbf{r}_{i+N_s} - \mathbf{r}_i - \mathbf{L}_x|$ of any particle – replicated particle pair when the self-similarity constraint is α and the temperature is β_α . In (14) this distribution function is evaluated at its ‘edge’ when $r = \alpha$.

However, in the limit $\alpha_1 \rightarrow 0$, we find that $4\pi g_\alpha(r) \alpha^2 / 3 \cong 1/\alpha$, and so greater numerical accuracy is achieved by integrating with respect to $\ln(\alpha)$. This transforms (14) to

$$\Delta(\beta F_\alpha) = -4\pi N_s \int_{\ln(\alpha_1)}^{\ln(\alpha_m)} d \ln(\alpha) g_\alpha(r = \alpha) \alpha^3 \quad (15)$$

Putting (8), (12), and (15) together gives our final result for the configurational contribution, which in terms of a length scale λ is

$$\frac{\Delta(\beta F)}{N_s} \cong -\ln\left(\frac{V_{\alpha_1}}{\lambda^3}\right) + \frac{1}{N_s} \int_{\beta_s/2}^{\beta_s} d\beta \langle H_\alpha \rangle - 4\pi \int_{\ln(\alpha_1)}^{\ln(\alpha_m)} d \ln(\alpha) g_\alpha(r = \alpha) \alpha^3 \quad (16)$$

which is exact in the limits $\alpha_1 \rightarrow 0$ and $\alpha_m \rightarrow \infty$. Obviously, for computer calculations finite limits need to be chosen for $\ln(\alpha_1)$ and $\ln(\alpha_m)$. For the upper limit, α_m is large enough when $g_{\alpha_m}(r = \alpha_m) \sim 0$. For a crystal there will always exist $\alpha_m < l$ for which this occurs, where l is the maximum lattice spacing in any direction. On the other hand, in general it is not known in advance how small α_1 needs to be for a desired level of accuracy. However, it is known that in the limit

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4 $\alpha_1 \rightarrow 0$, we find $4\pi g_\alpha(r = \alpha)\alpha^3 \rightarrow 3$. A sensible strategy then is to start with $\alpha_m = l$ and to reduce
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6 $\ln(\alpha)$ in a sequence of steps until this limit is reached with sufficient accuracy, i.e. until equation (16)
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8 has converged. Figure 3 shows how $4\pi g_\alpha(r = \alpha)\alpha^3$ depends on α for a hard sphere face-centred-
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10 cubic crystal with reduced density $\rho^* = \rho\sigma^3 = 1.04086$, where σ is the hard sphere diameter.

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16 To calculate the integrals in (16) a series of simulations for a range of values of α must be performed.
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18 Each simulation is essentially an ordinary canonical ensemble Monte-Carlo simulation of the double-
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20 size system, except that the constraint on the configurational Hamiltonian defined in (5), which
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22 depends on α , must be included. It is important to perform compound MC moves to ensure efficient
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24 sampling when α is small. These moves are described in the earlier work¹⁻³ in detail, but briefly they
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26 consist of simultaneous trial moves for both particle i and its partner, $i+N_s$. A trial move consists of
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28 displacing both particles by the same (large) amount, and then displacing one of them a (small)
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30 amount more. Recall particle 1 is clamped and so is never displaced. Also, the temperature path from
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32 $\beta_s/2$ to β_s needs to be defined. In fact this path will depend on α . In paper 1 a suitable path is found to
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34 be one that keeps the total average configurational energy, $\langle H_\alpha \rangle$, nearly constant as α changes. An
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36 algorithm for choosing β_α that achieves this is defined in that work, although it is not unique and
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38 many other algorithms can be defined. This kind of path, i.e. one that keeps the configurational energy
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40 nearly constant, is thought to work well because it is important to avoid any potential phase
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42 transitions. A phase transition could occur if the pressure of the double-size constrained system for
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44 any particular value of α changes substantially from that of the unconstrained system. And this can
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46 happen if the average energy of the double-size constrained system changes substantially from that of
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48 the unconstrained system. So a temperature path that keeps the average configurational energy nearly
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50 constant appears to be suitable.

51 52 53 54 55 56 57 58 **2.2 Rigid linear molecules**

Equation (16) is valid only for spherical particles, which include hard spheres and Lennard-Jones particles. In paper 1 it was shown how the SR method can be extended to rigid linear molecules, such as needles and dumbbell shaped molecules, and results obtained for hard and Lennard-Jones dumbbells compared well with reference data in the literature⁴⁸⁻⁵⁰. To make the extension to rigid linear molecules we first have to consider and describe the degrees of freedom of such a molecule. In addition to the position of the molecular centre, the direction of a rigid linear molecule can be described in terms of Euler angles, i.e. θ describes its polar angle (the angle between a molecule's director and the z-Cartesian axis) and ϕ describes its azimuthal angle (the angle formed by the projection of the director onto the x-y plane and the x-axis). The z-axis and x-axis referred to here are fixed in space. However, when using the SR method it is convenient to express the orientational coordinates of each replicated molecule with respect to the coordinates of that molecule's original partner molecule. So, for each replicated molecule τ is the angle between the directors of a replicated molecule and its partner, while φ is the azimuthal angle of a replicated particle with respect to coordinates fixed to the director of the original particle. Using this convention, which is described in detail in terms of rotation matrices in paper 1, the Hamiltonian for the constrained double-size system can now be written as

$$H_{\alpha}(r^{N_d}, V_d) = H_0(r^{N_d}, V_d) + \sum_{i=1}^{N_r} \phi(r_i - \alpha) + \sum_{i=1}^{N_r} \phi(\eta_i - \hat{\eta}_{\alpha}) \quad (17)$$

where $\eta_i = 1 - \cos(\tau_i)$ and $\hat{\eta}_{\alpha} = \hat{\eta}(\alpha)$ is the constraint on each η_i . Recall, this constraint is effectively on the angle τ_i between the directors of each replicated particle and its original partner. So each replicated particle's director can point anywhere within a circle on the surface of the unit sphere centred on the director of the original particle. These constraints are illustrated in Figure 4. Using this convention it is once more straightforward to derive the corresponding replication and relaxation terms following the same procedure as for positional degrees of freedom. The corresponding free energy expression for rigid linear molecules is

$$\frac{\Delta(\beta F)}{N_s} = -\ln\left(\frac{V_{\alpha_1} V_{\eta_1}}{\lambda^3}\right) + \frac{1}{N_s} \int_{\beta_s/2}^{\beta_s} d\beta_{\alpha} \langle H_{\alpha} \rangle - 4\pi \int_{\ln(\alpha_1)}^{\ln(\alpha_m)} d \ln(\alpha) g_{\alpha}(r = \alpha) \alpha^3 - \int_{\ln(\hat{\eta}_1)}^{\ln(\hat{\eta}_m)} d \ln(\hat{\eta}) g_{\hat{\eta}_\alpha}(\eta = \hat{\eta}_\alpha) \hat{\eta}_\alpha \quad (18)$$

where $V_{\eta_1} = 2\pi\hat{\eta}_1$ is the phase space volume (solid angle) available to each replicated particle when fully constrained, and $g_{\hat{\eta}_\alpha}(\eta)$ is the average ‘partner’ distribution function $g_{\hat{\eta}_\alpha}(\eta) = N_s^{-1} \sum_i g_{\hat{\eta}_\alpha}(\eta_i = \eta)$, where $g_{\hat{\eta}_\alpha}(\eta_i)$ is the individual η partner distribution function for any particle – replicated particle pair when the constraint is $\hat{\eta}_\alpha$ and the temperature is β_α (see Figure 4).

In (18) this distribution function is evaluated at its ‘edge’ when $\eta = \hat{\eta}_\alpha$.

The upper limit, $\hat{\eta}_m$, depends on the kind of particle and crystal phase being studied. For molecules with an inversion centre (e.g. homonuclear dumbbells) the maximum value for $\hat{\eta}_m$ is 1, and for plastic crystals (these are crystals without long-range orientational order) it is important to use this maximum limit. However, for orientationally ordered crystals of these molecules $\hat{\eta}_m$ is large enough when $g_{\hat{\eta}_m}(\eta = \hat{\eta}_m) \sim 0$. On the other hand, for plastic crystals composed of molecules without an inversion centre (e.g. heteronuclear dumbbells) it is important to set $\hat{\eta}_m = 2$. Finally, for orientationally ordered crystals composed of these molecules $\hat{\eta}_m$ is again large enough when $g_{\hat{\eta}_m}(\eta = \hat{\eta}_m) \sim 0$. However, one also has to ensure that all the possible permutations for ‘up’ and ‘down’ molecules are properly sampled. This is similar to the problem of residual entropy for water ice⁵. If we now consider $\hat{\eta}_1$, it is small enough when $g_{\hat{\eta}_1}(\eta = \hat{\eta}_1) \hat{\eta}_1 \sim 1$. Clearly, the functional form for $\hat{\eta}(\alpha)$ should be chosen to reproduce these limits, and in paper 1 a simple linear relationship is found to be sufficient. Figure 5 shows how $g_{\hat{\eta}_\alpha}(\eta = \hat{\eta}_\alpha) \hat{\eta}_\alpha$ depends on $\hat{\eta}_\alpha$ for an α -N₂ face-centred-cubic¹ crystal of hard dumbbells with reduced bond length $L^* = L/\sigma = 0.3$ and reduced molecular density $\rho^* = \rho\sigma^3 = 0.883397$, where σ is the diameter of one site of the dumbbell.

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In paper 1 the (configurational) canonical Helmholtz free energy difference (18) for some face-centred-cubic crystals composed of hard and Lennard-Jones dumbbells was evaluated for several different systems, including some orientationally ordered and plastic crystals, and in general the results compared well with values for the absolute canonical Helmholtz free energy obtained using an Einstein crystal (Frenkel-Ladd) based approach⁴⁸⁻⁵⁰. Serious disagreement between the SR and FL approaches was found only for one of the LJ dumbbell systems.

2.3 Extension to other molecules and ensembles

We see by comparing (16) and (18) how a general expression for the free energy of arbitrary space-filling crystals can be developed. There is a contribution to the replication term from each degree of freedom corresponding to the phase space volume available to a replicated particle when the system is most constrained at $\alpha = \alpha_1$. For rigid molecules there is a contribution due to the translational degrees of freedom of the molecular centre ($V_{\alpha_1} = 4\pi\alpha_1^3/3$). For rigid linear molecules there is an additional contribution due to the solid angle described by a molecule's director which, because only the relative polar angle needs to be constrained for these molecules (since the Hamiltonian is essentially independent of the relative azimuthal angle when the polar angle is very small), is $V_{\hat{\eta}_1} = 2\pi\hat{\eta}_1$. For general rigid molecules without any internal symmetries we expect an additional contribution due to a constraint on internal molecular rotations about the major axis, described by $-\pi \leq \kappa \leq \pi$, equal to $V_{\hat{\kappa}_1} = 2\hat{\kappa}_1$, where $\hat{\kappa}_1$ is the initial constraint on $|\kappa|$. Once again, for the same reason given above, it should not be necessary to constrain the relative azimuthal angle, and so $V_{\hat{\eta}_1}$ remains equal to $2\pi\hat{\eta}_1$.

For non-rigid molecules there is some freedom in the description of the molecular degrees of freedom. For example, for a non-rigid homonuclear dumbbell molecule one could choose to describe a molecule either in terms of the position of the molecular centre, the orientation of the molecular director and the bond length, or alternatively in terms of the positions of the two sites. Because with the SR method it is convenient to express the coordinates of each replicated particle relative to those

of each corresponding original particle, a replicated particle could be described in terms of either r_i , η_i , ϕ_i and the difference in bond length, or alternatively in terms of the positions of the two sites relative to those of the original molecule. Each choice will lead to different expressions for both the replication and relaxation terms, but of course the free energies calculated by either choice should be the same.

In general, we can expect the replication term for a pure crystal to be given by the analytic expression

$$\Delta(\beta F_{rep}) = -N_s \ln\left(\frac{\Psi_1}{\lambda^d}\right) \quad (19)$$

where $\Psi = \prod_j f_j(\hat{r}_j)$ is the phase-space available to a single particle (which is just the product of the phase space functions $f_j(\hat{r}_j)$ for each degree of freedom r_j , while $\Psi_1 = \prod_j f_j(\hat{r}_{j1})$ is the phase-space volume available to each replicated particle when the system is fully constrained, and d is the dimensionality of the crystal.

By comparing (16) and (18) we see that for each degree of freedom relaxed during the relaxation step that there is an integral over its respective partner distribution function. Each corresponding integrand is multiplied by the rate of change of the phase space volume, so we expect the replication term can be generalised to

$$\Delta(\beta F_{rel}) = \int_{\beta_s/2}^{\beta_s} d\beta_\alpha \langle H_\alpha \rangle - \sum_{j'} \int_{\ln(\hat{r}_{j1})}^{\ln(\hat{r}_{jm})} d \ln(\hat{r}_{j\alpha}) g_{\hat{r}_{j\alpha}}(r_j = \hat{r}_{j\alpha}) \hat{r}_{j\alpha} \left. \frac{d\Psi}{d\hat{r}_j} \right|_{\hat{r}_{j\alpha}} \quad (20)$$

where the sum need only be over those degrees of freedom that were constrained upon replication, indicated by j' , and hence need to be relaxed. In addition, as with water ice, any kind of residual entropy would need to be accounted for.

The sum of (19) and (20) gives a rather compact and simple expression for the Helmholtz free energy of crystals

$$\frac{\Delta(\beta F)}{N_s} = -\ln\left(\frac{\Psi_1}{\lambda^d}\right) + \int_{\beta_s/2}^{\beta_s} d\beta_\alpha \langle H_\alpha \rangle - \sum_{j'} \int_{\ln(\hat{r}_{j1})}^{\ln(\hat{r}_{jm})} d \ln(\hat{r}_{j\alpha}) g_{\hat{r}_{j\alpha}}(r_j = \hat{r}_{j\alpha}) \hat{r}_{j\alpha} \left. \frac{d\Psi}{d\hat{r}_j} \right|_{\hat{r}_{j\alpha}} \quad (21)$$

Because the replication term is analytic only one kind of simulation is needed that measures the respective partner distribution functions at their ‘edges’, $g_{\hat{r}_{j\alpha}}(r_j = \hat{r}_{j\alpha})$, and the average configurational energy, $\langle H_\alpha \rangle$, for a suitable range of values of the relaxation parameter α , and for a suitable β -path. The corresponding generalised Hamiltonian for these constrained double-size simulations can be defined as

$$H_\alpha(\{\mathbf{r}\}^{N_d}, V_d) = H_0(\{\mathbf{r}\}^{N_d}, V_d) + \sum_{j'} \sum_{i=1}^{N_s} \phi(r_{ij} - \hat{r}_{j\alpha}) \quad (22)$$

where $\{\mathbf{r}\}^{N_d}$ indicates all particle coordinates (positions, orientations etc.), and r_{ij} is the j th constrained degree of freedom, corresponding to the constraint $\hat{r}_{j\alpha}$, which depends on the difference between the coordinates of an original particle i and its replicated partner $i+N_s$.

At no point have any assumptions about the nature of molecule – molecule interactions or the presence of an external field been made (except that any external field should have the same translational symmetry as the single-size simulation cell in the replication direction), and so, without

any change in the technique, it is expected that the SR method can be applied to systems involving pairwise or higher body interactions and to systems involving external fields, such as pore walls, provided they have the required translational symmetry. Clearly, further work is needed to confirm these expectations.

Another attractive feature of the SR method is that the centre of mass is not constrained, and so no centre of mass corrections⁴² are needed. Also, it was shown in paper 2 that the SR method can be used with the isothermal-isobaric ensemble. For these simulations all quantities become ensemble averaged with respect to volume fluctuations. The reduced Gibbs free energy difference, $\Delta(\beta G)$ for spherical particles was obtained as

$$\frac{\Delta(\beta G)}{N_s} \cong -\ln \left\langle \frac{V_{\alpha_1}}{\lambda^3} \right\rangle_s - \frac{\ln(2)}{N_s} + \frac{1}{N_s} \int_{\beta_s/2}^{\beta_s} d\beta \langle P_s V_d + H \rangle_\alpha - 4\pi \int_{\ln(\alpha_1)}^{\ln(\alpha_m)} d \ln \alpha \left\{ g_\alpha(r = \alpha L_x) \alpha^3 L_x^3 \right\}_\alpha \quad (23)$$

Here, there are several new terms and some new notation that require explanation. But first, an important difference between this isothermal-isobaric ensemble derivation and the canonical ensemble derivation must be described. This difference concerns the Hamiltonian for the constrained double-size system, which for spherical particles is now written

$$H_\alpha(r^{N_d}, V_d) = H_0(r^{N_d}, V_d) + \sum_{i=1}^{N_s} \phi(r_i - \alpha L_x) \quad (24)$$

Note the factor L_x . Although important, it is actually quite trivial to implement this constraint and clearly it is possible to define the constrained Hamiltonian in this way for the canonical version as well. So this can be considered a generalised form of the self-similarity constraint. Inclusion of this factor in (24) allows the self-similarity constraint to fluctuate in tandem with the volume. This difference ensures that volume fluctuations are not biased by the self-similarity constraint (actually, this form of the Hamiltonian assumes that volume fluctuations occur via Monte-Carlo moves that

uniformly scale the volume, which is acceptable provided the shape of the simulation cell is already consistent with the equilibrium shape of the crystal unit cell). Switching α for αL_x also results in α^3 becoming $\alpha^3 L_x^3$ in the right most term in (23), and in V_{α_1} becoming $4\pi\alpha^3 L_x^3/3$. Also note the appearance of a $\ln(2)$ term and the term $P_s V_d$, where P_s is the pressure and V_d is the volume of the double-size system. The final difference is that each term on the right hand side of (23) is an ensemble average. The angle brackets denote an ensemble average with respect to all fluctuations. But because g_α is already an ensemble average with respect to particle positions, the curly brackets denote a further ensemble average of g_α only with respect to volume fluctuations.

Another important practical difference in evaluating (23) compared to (16) concerns how the β -path is defined during relaxation, that is how temperature is adjusted during relaxation. The canonical ensemble version employs an algorithm that attempts to keep the average (configurational) energy of the double-size system nearly constant during relaxation. As explained earlier, the rationale for this is that if the average energy is roughly constant during relaxation then the pressure might also be nearly constant, and so the crystal should not undergo any change of phase. However, with the isothermal-isobaric version an algorithm can be designed that works directly with the volume. That is, in paper 2 an algorithm is employed that attempts to keep the average volume nearly constant during relaxation. It is not clear whether this choice for the β -path is important, or whether the nearly constant average energy algorithm would also be suitable for the isothermal-isobaric version.

Following the same arguments that lead to (21), the general expression for the Gibbs free energy difference is

$$\frac{\Delta(\beta G)}{N_s} \cong -\ln \left\langle \frac{\Psi_1}{\lambda^3} \right\rangle_s - \frac{\ln(2)}{N_s} + \frac{1}{N_s} \int_{\beta_s/2}^{\beta_s} d\beta \langle P_s V_d + H \rangle_\alpha - \sum_{j'} \int_{\ln(\hat{r}_{j1})}^{\ln(\hat{r}_{jm})} d \ln \hat{r}_j \left\{ g_{\hat{r}_j}(r_j = \hat{r}_j) \hat{r}_j \frac{\partial \Psi}{\partial \hat{r}_j} \right\}_\alpha \quad (25)$$

where for any positional degree of freedom we must let the self-similarity constraint fluctuate in tandem with the volume. Once again, this expression does not account for any residual entropy. Future work will aim to test this result.

3 The Gibbs ensemble adapted to crystalline solid – fluid coexistence

A fluid system with fixed volume at sub-critical temperature and density between the coexisting vapour and liquid densities will spontaneously phase separate to form the corresponding vapour and liquid phases because this macrostate has the lowest Helmholtz free energy. A state with even lower free energy is one without a vapour-liquid interface. While it is not possible to avoid the formation of an interface in nature under these circumstances, it is possible to do this in molecular simulations, and this is the basis of the NVT Gibbs ensemble simulation method⁶⁻⁸. The advantage this affords is that the uniform bulk phases at coexistence can be simulated, and this requires far fewer particles than a simulation with an interface if accurate bulk fluid properties are required. Since its invention this technique has become a very popular method⁵¹ for determining fluid-fluid coexistence. Unfortunately, for the reason outlined in section 1.2, it is, in principle, impossible to perform Gibbs ensemble simulations when one of the phases is a crystalline solid in a direct way. However, it is possible to perform these simulations in an indirect way, and this section summarizes work⁴ that demonstrates this.

Once again, we start by considering the configurational partition function of a pure system, this time for a ‘two box’ simulation where box 1 contains crystalline solid and box 2 contains fluid, both with periodic boundaries

$$\Psi = \sum_{N_1=0}^N \int dV_1 \int \frac{d\mathbf{r}^{N_1}}{N_1!} \exp(-\beta H(\mathbf{r}^{N_1}, V_1)) \int \frac{d\mathbf{r}^{N_2}}{N_2!} \exp(-\beta H(\mathbf{r}^{N_2}, V_2)) \quad (26)$$

Here, \mathbf{r} represents all molecular degrees of freedom, i.e. position, orientation etc., and for an NVT Gibbs simulation we have $V = V_1 + V_2$ and $N = N_1 + N_2$. The key idea of paper 4 is to replace the

crystalline solid simulation box by a free energy model of the crystalline solid, i.e. to rewrite the partition function as

$$\Psi = \sum_{N_1=0}^N \int dV_1 \exp(-\beta F(N_1, V_1)) \int \frac{d\mathbf{r}^{N_2}}{N_2!} \exp(-\beta H(\mathbf{r}^{N_2}, V_2)) \quad (27)$$

where $F(N_1, V_1)$ is the canonical Helmholtz free energy for a system with N_1 molecules in volume V_1 . Provided F is known accurately for all values of N_1 and V_1 that are sampled during a simulation, then ensemble averages can be calculated accurately for either phase, provided the fluid can be simulated in box 2. Mehta and Kofke⁵² used a similar idea in their application to vapour-liquid coexistence at low temperatures by employing a free energy model for a low density vapour phase in coexistence with a simulated liquid phase.

To make progress, a free energy model of the crystalline solid phase is required for all values of N_1 and V_1 likely to be sampled during a Gibbs simulation. Generally, a free energy model can be obtained as follows. First, a Taylor series expansion in inverse powers of the number of molecules, $\delta = 1/N$, for the free energy per particle $f_\rho = F(N, N/\rho)/N$ at a particular density ρ , can be written

$$f_\rho(\delta_1) = f_\rho(0) + \delta_1 \left. \frac{\partial f_\rho}{\partial \delta} \right|_{\delta=0} + O(\delta_1^2) \quad (28)$$

From this, it follows immediately that

$$f_\rho(\delta_1) \approx f_\rho(\delta_c) + (\delta_1 - \delta_c) \left. \frac{\partial f_\rho}{\partial \delta} \right|_{\delta=0} \quad (29)$$

and hence the canonical Helmholtz free energy for a system with N_1 particles in volume V_1 can be written in terms of the canonical Helmholtz free energy of a system with N_c molecules at the same density as

$$F(N_1, V_1) \approx \frac{N_1}{N_c} F(N_c, V_1 \frac{N_c}{N_1}) + \left(1 - \frac{N_1}{N_c}\right) \left. \frac{\partial f_p}{\partial \delta} \right|_{\delta=0} \quad (30)$$

which is accurate for sufficiently large N_1 and N_c . This analysis has simplified the problem from that of knowing the free energy for each combination of N_1 and V_1 to instead just knowing the free energy for a fixed number of molecules, N_c , in a range of volumes, and the constant $(\partial f_p / \partial \delta)_{\delta=0}$. In paper 2 equation (30) is truncated at its first term resulting in a simple linear scaling approximation for F

$$F(N_1, V_1) \approx \frac{N_1}{N_c} F(N_c, V_1 \frac{N_c}{N_1}) \quad (31)$$

leaving just $F(N_c, V)$ to be determined for a range of values of V . This function can be found from the volume probability distribution function, $p(V)$, of an isothermal-isobaric (NPT) simulation with N_c particles at pressure P

$$F(N_c, V) = -k_B T \ln p(V) - PV + \mu N_c \quad (32)$$

where μ is the chemical potential corresponding to this pressure (note the sign error in equation (16) in paper 4). To use (31) a pressure should be chosen such that the range of densities sampled during the NPT simulation is similar to that sampled during the Gibbs simulation. The chemical potential at this pressure must also be known, and this can be determined by any free energy method for crystalline solids, including the SR method described in the preceding sections. In paper 4, for convenience, a pressure for which i) the chemical potential was already known, and ii) it was also

known that the appropriate range of densities would be sampled, was chosen. However, in general, an appropriate pressure is not usually known in advance, and so several iterations of this Gibbs simulation technique might be required to obtain convergent results. Future work will test this aspect of this method.

In paper 4 a free energy model for the face centred cubic phase of a crystalline (shifted force) Lennard-Jones system was generated by combining (31) and (32) to obtain

$$F(N_1, V_1) = \frac{-k_B T N_1}{N_c} \ln p\left(V_1 \frac{N_c}{N_1}\right) - P V_1 + \mu N_1 \quad (33)$$

This free energy model, when combined with (27), enabled Gibbs ensemble simulations of both vapour – solid and liquid – solid coexistence at the triple point of this Lennard-Jones system. The known pressure and chemical potential at this point were used to generate the free energy for $N_c = 256$ particles at this state. This data is shown in Figure 6, and is used as input to (31). Using this free energy model, good agreement was found for the density, pressure and chemical potential of the coexisting phases at the triple point between the indirect Gibbs simulations described here and from reference values in the literature⁵³ (to within statistical error).

Clearly, this approach is not as convenient as standard Gibbs simulations for gas-liquid coexistence because usually a suitable pressure and chemical potential at which to generate the canonical Helmholtz free energy model via NPT simulation is not known in advance. In paper 4 a state point for which this data was known in advance was specifically chosen for convenience to test the method. But usually this information will not be known. Also, this method is less convenient than standard Gibbs simulations of vapour-liquid coexistence because several types of simulation are needed to generate the free energy model, including a free energy calculation for the crystalline solid. Future work will aim to compare this indirect Gibbs ensemble strategy with the usual alternative strategy, which is calculation of the free energy along both solid and fluid branches near coexistence⁵. Also

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3 note the work of Chen et.al.⁵⁴ concerning simulation of fluid-solid coexistence. Their Gibbs
4 simulation technique is designed to allow simulation of phase coexistence between liquid and solid
5 phases. However, in their work equilibrium between the liquid phase and the solid phase is achieved
6 via a liquid – solid interface. So, the title of their paper is not strictly accurate. Nevertheless, despite
7 the fact that their method requires many more particles due to the presence of an interface, it could be
8 quite convenient.
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18 Despite the initial success of the indirect Gibbs simulation technique summarized above, several
19 problems with this method should be highlighted. First, as with any Gibbs simulation, it becomes very
20 slow if the liquid phase is dense because the probability of a successful particle exchange between
21 boxes becomes very low. In this case specialized ‘biasing’ techniques⁹ might be useful. Second, if the
22 density difference between coexisting phases is small, which is often the case for coexisting liquid
23 and solid phases, then large fluctuations in the number of particles in each box should occur. In this
24 case very long simulations are needed to ensure sufficient sampling of these large fluctuations. In
25 addition, a more accurate approximation than (33) for the free energy model might be needed. This
26 model relies on the simple linear scaling approximation (31), which is expected to lose accuracy
27 when either N_c or N_l are small. A more sophisticated approach could use both the first and second
28 terms in (30), with at least two NPT simulations performed at the same pressure, but with
29 significantly different numbers of particles, to determine $(\partial f_p / \partial \delta)_{\delta=0}$. Finally, this approach has, so
30 far, only been applied to pure crystals and it is not yet clear if crystalline mixtures can be simulated in
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Figures

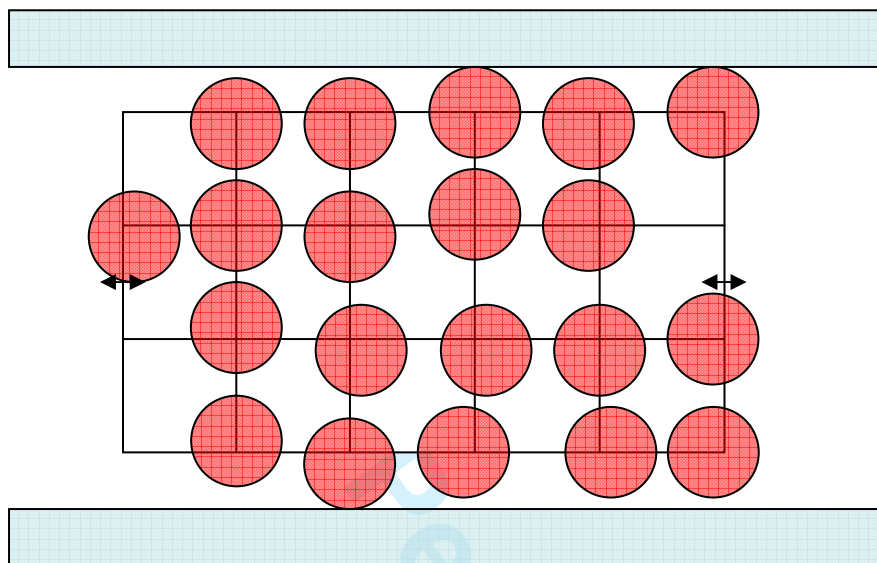


Figure 1. Sketch of the $N\sigma T$ ensemble for simulation of crystalline solid in a slit pore. Fluctuations in volume are allowed in the direction of the slit pore to equilibrate the interfacial tension, σ . Periodic boundaries are applied in directions parallel to the pore walls.

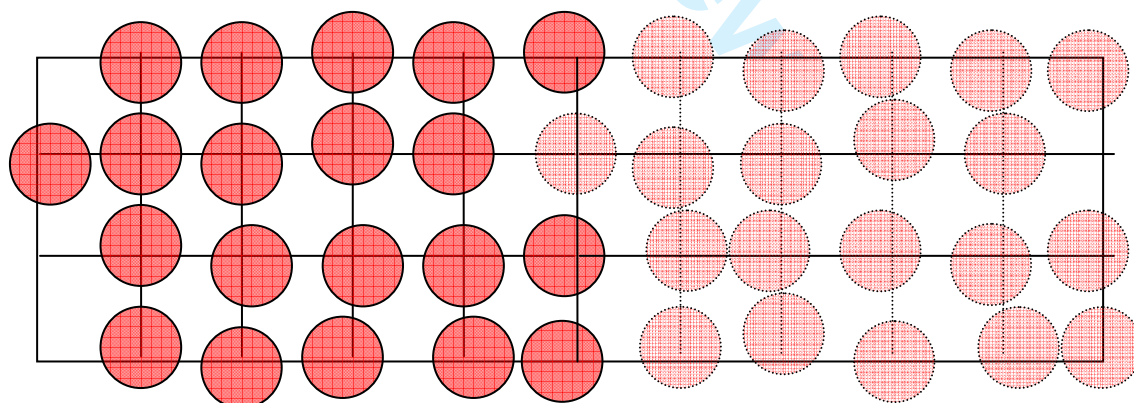


Figure 2. Sketch of the basic idea behind the self-referential method; the Gibbs free energy of the double-size system is twice that of a single-size system. Note that these are not isolated systems; periodic boundaries are applied.

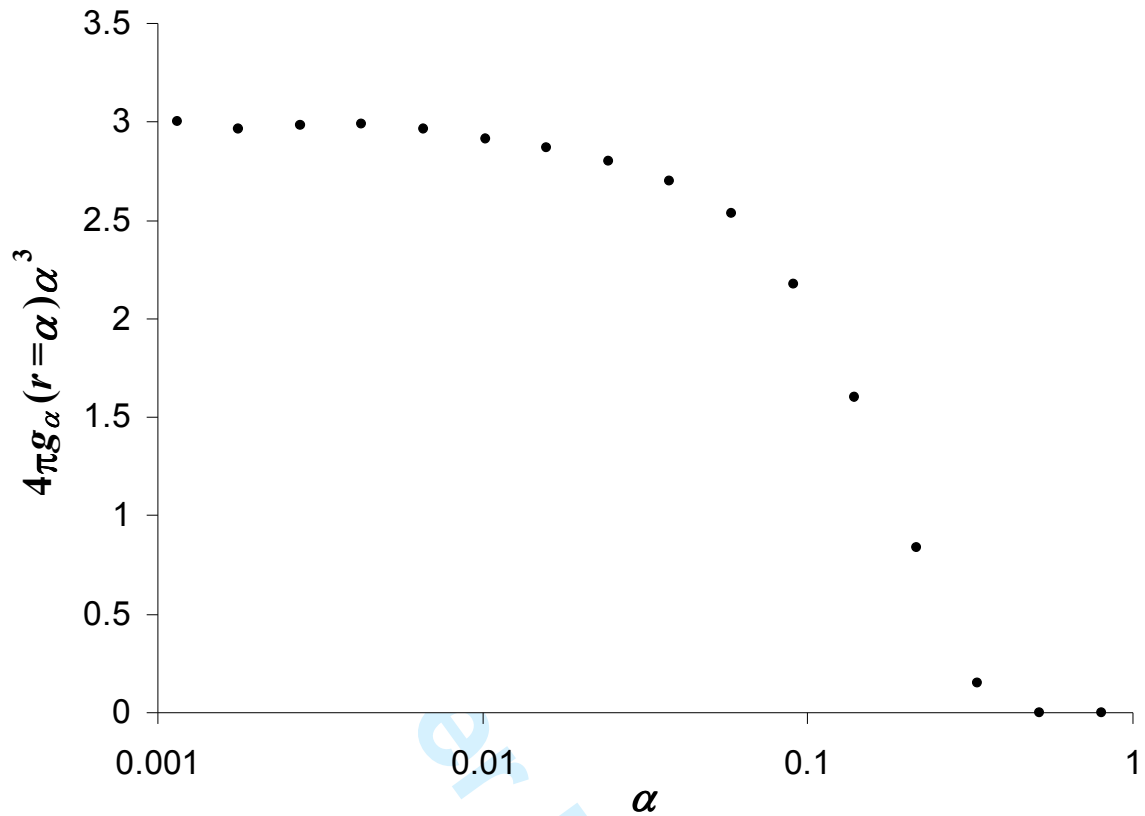


Figure 3. The variation of $4\pi g_\alpha(r=\alpha)\alpha^3$ with α for a hard sphere fcc crystal with reduced density (average number of hard spheres per hard-sphere diameter cubed) 1.04086. Symbol sizes are larger than the standard error, and α is on a logarithmic scale.

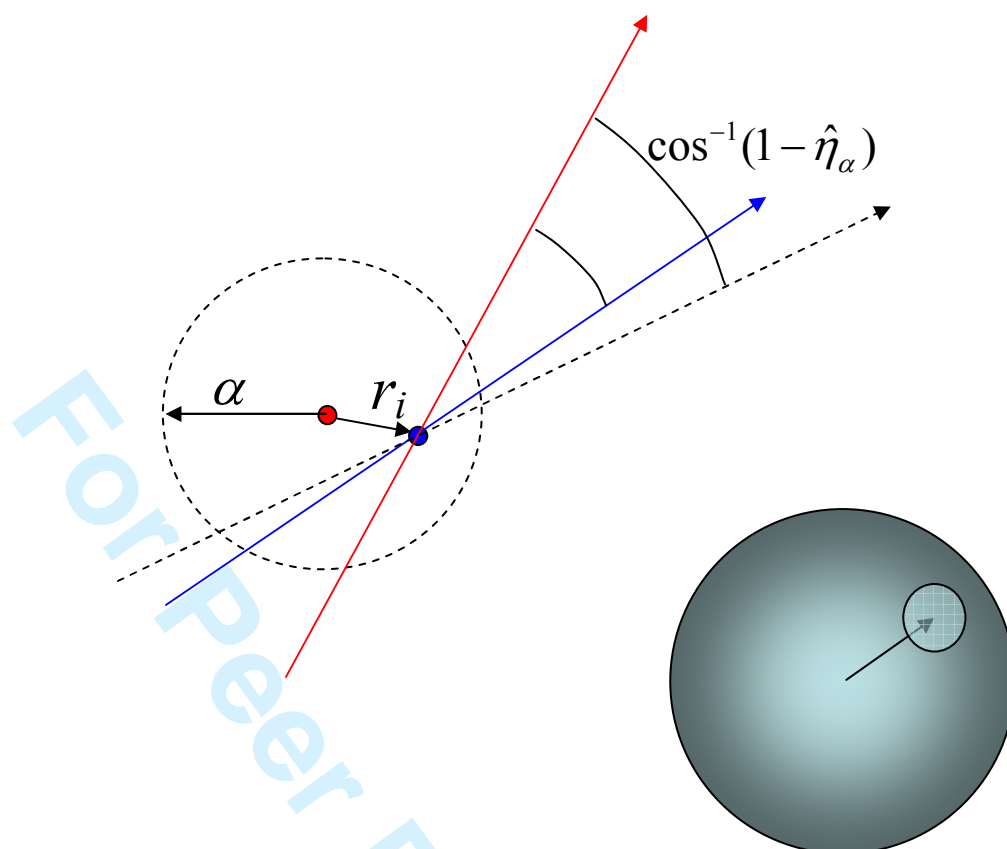


Figure 4. Depiction of some terms used to describe the relative positions of the i th rigid linear molecule and its replicated partner. The red and blue dots are the centres of the original and replicated partner dumbbells respectively (after subtracting the replication vector \mathbf{L}_x from the position of the replicated dumbbell), while the red and blue lines are the directors of the original and replicated partner dumbbells respectively. r_i , the relative separation of their centres is constrained to be less than α , while τ_i , the angle between their directors, is constrained to be less than $\cos^{-1}(1 - \hat{\eta}_\alpha)$. The relative azimuthal angle is not constrained, so the director of the replicated molecule can point anywhere within a circle on a sphere centred on the director of the original molecule.

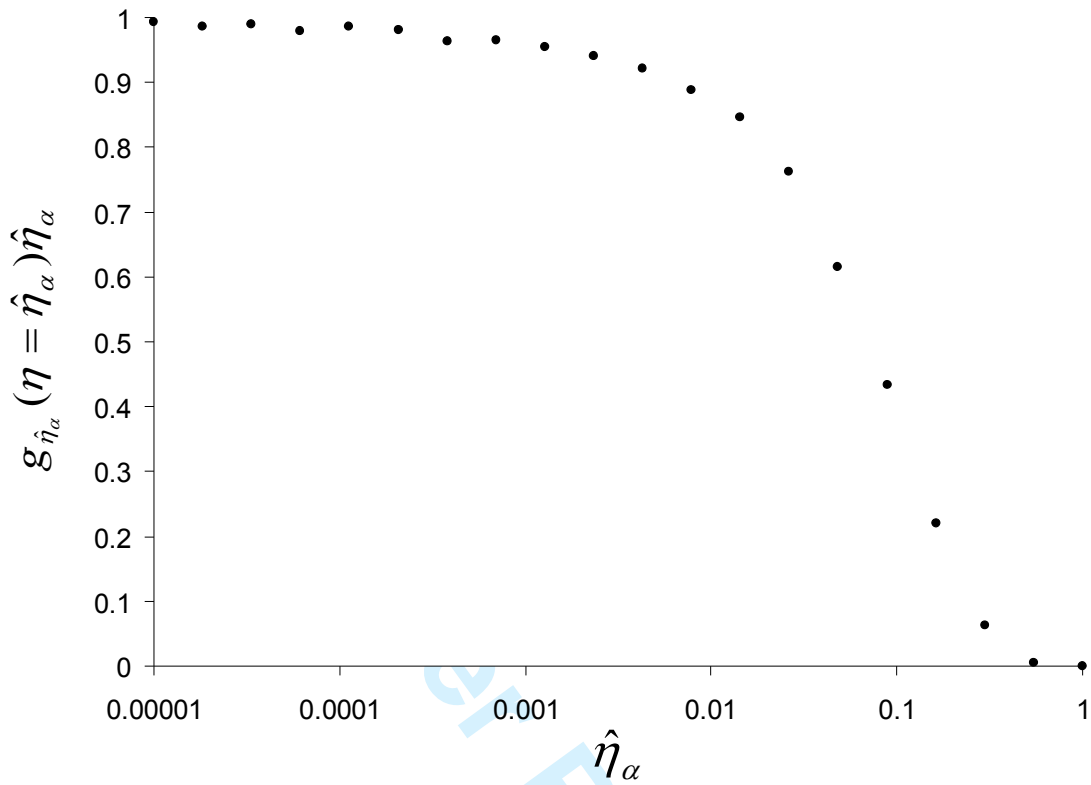


Figure 5. The variation of $g_{\hat{\eta}_\alpha}$ with $\hat{\eta}_\alpha$ for a hard face centred cubic hard dumbbell crystal with reduced bond length $L^* = L/\sigma = 0.3$ and reduced molecular density $\rho^* = \rho\sigma^3 = 0.883397$, where σ is the diameter of one site of the dumbbell.

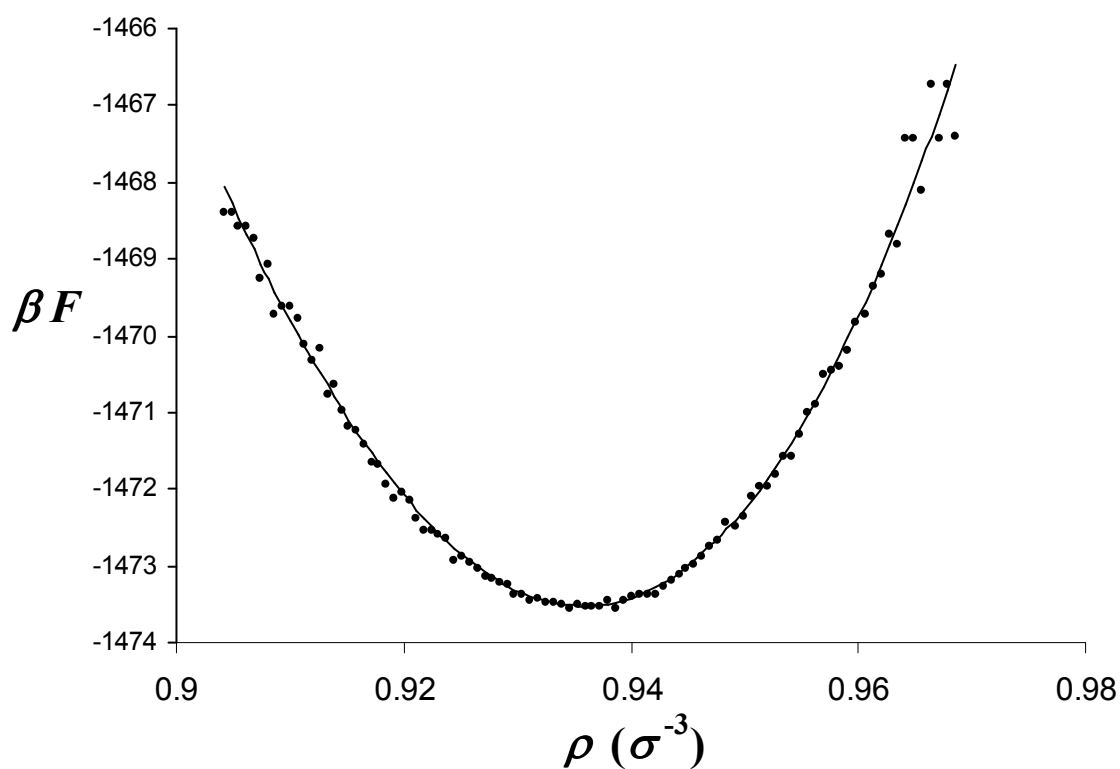


Figure 6. Reduced canonical Helmholtz free energy for the crystalline solid phase of a shifted-force Lennard-Jones system with 256 particles for a range of densities ρ at reduced temperature $T^* = (\beta\varepsilon)^{-1} = 0.56$, reduced pressure $P^* = P\sigma^3/\varepsilon = 0.00186$, and reduced configurational chemical potential $\mu^* = \mu/\varepsilon = -3.23$, where σ and ε are the Lennard-Jones length and energy parameters respectively. The symbols are simulation data, while the line is a cubic polynomial fit to this data and is used to generate the free energy model for use in the indirect Gibbs simulation described in the text.

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