Simulating fluid-crystalline solid equilibria with the Gibbs ensemble

M.B. Sweatman and N. Quirke

Department of Chemistry, Imperial College, South Kensington, London, UK. SW7 2AY.

Abstract

We employ the Gibbs ensemble to simulate gas-liquid-solid equilibrium at the triple-point of a shifted-force Lennard-Jones system. This is made possible by generating an accurate canonical Helmholtz free-energy model of the (defect-free) solid phase. This free-energy model is generated by a single isothermal-isobaric simulation at a pressure not too far from coexistence for which the chemical potential is known. We also discuss the merits of our methods, compared to others in the literature, for simulating crystals in confined geometries.

Introduction

There are several ways to determine phase coexistence for a bulk system using Monte-Carlo simulation. A popular method[1] calculates a free-energy density model for each phase at the same temperature along both phase branches in the vicinity of the transition. Coexistence is then easily determined by finding the point at which the branches cross. A problem with this method is the effort required to calculate the free-energy density models, since many simulations and thermodynamic integration may be required. Alternatively, one could employ a non-Boltzmann sampling scheme[1, 2], or a phase switch approach[3, 4], that calculates the free-energy *difference* between the two competing phases under given conditions. However, these approaches can also require considerable effort because it is usually necessary to repeat these simulations several times in order to interpolate the location where the branches cross. In the case of a non-Boltzmann sampling scheme considerable effort might also be required to connect each phase with a continuous path in order-parameter space. Alternatively, a much larger canonical system that incorporates a phase interface can be simulated[5, 6]. Hence the popularity of the Gibbs ensemble[7, 8]. Its main advantages are that coexisting states are generated spontaneously during a single simulation (given reasonable initial conditions) and that relatively small systems can be simulated since a phase interface is not required.

Now consider these methods in the context of phase coexistence in confined geometries (in slit pores for example). For confined systems it can be considerably more difficult to define a suitable thermodynamic integration path that does not cross any first-order phase boundaries than for the bulk case because of potential surface induced phase transitions. Two approaches can be adopted in the case of a non-Boltzmann sampling method; either simulate in the grand canonical ensemble or simulate in the isothermal-isobaric ensemble and employ a suitable method for calculating the chemical potential so that a phase diagram can be drawn (chemical potential is identical in bulk and confined phases at equilibrium). We are limited to the isothermal-isobaric ensemble if using a phase-switch method. The Gibbs ensemble has also been applied[8, 9] to confined systems.

Now consider fluid-crystalline solid coexistence in confined geometries. Special techniques[1, 10, 11] are needed to calculate the free-energy density model of the crystal phase, and it can be an even greater problem to define the thermodynamic integration path. The grand-canonical non-Boltmann sampling approach cannot be used because of the problem with defects (discussed later), and the isothermal-isobaric non-Boltzmann and phase switch methods can only be used if the chemical potential of the fluid phase can be calculated since there are currently no direct methods (that avoid thermodynamic integration) for calculating the chemical potential of crystalline solids. The conventional Gibbs ensemble method fails for the same reason as the grand-canonical non-Boltzmann method, i.e. particle creation/deletion in the crystal phase leads to defects.

The problem with grand canonical ensemble simulation of crystalline solids deserves some discussion. Radhakrishnan and colleagues[12, 13] have employed umbrella sampling (a.k.a. a Landau free-energy method) in the grand canonical ensemble extensively to determine fluid-solid coexistence for Lennard-Jones systems in slit pores. They show how freezing depends on pore width and fluid-solid interaction strength. However, let us consider a crystalline state with N_l lattice positions and N_d defects (either interstitials or vacancies) in a grand canonical ensemble. Particle fluctuations can occur only via the insertion or deletion of particles. Since the lattice is fixed in this simulation at constant volume, V, only fluctuations in N_d can occur. Since the chemical potential is the difference in canonical Helmholtz free-energy between states that differ by one particle at constant volume, $\mu = F(N+1,V,T) - F(N,V,T)$, and only defect fluctuations can occur in the simulation, then the chemical potential in their simulation is the chemical potential of defects – not the true chemical potential which has a contribution from lattice site fluctuations as well. So the work of Radhakrishnan and colleagues is flawed in this respect, i.e. the chemical potential in their work is $F(N_l,N_d+1,V,T) - F(N_l,N_d,V,T)$ whereas it should be $F(N_l+1,N_d,V,T) + F(N_l,N_d+1,V,T) - F(N_l,N_d,V,T)$. The missing contribution arises from particle fluctuations due to phonons, a problem that is not assuaged by analysing finite size effects. The severity of this problem depends on the relative magnitude of these contributions.

So, to determine fluid – solid crystal coexistence in the bulk or in confined geometries the most sensible options appear to be umbrella or phase switch sampling in the isothermal-isobaric ensemble, provided the chemical potential of the fluid phase is easily calculated. Here, we show how the Gibbs ensemble can be revived to treat this problem as well, at least for pure crystals of the type described above.

Three-phase coexistence and the Gibbs ensemble

Our method depends on generation of an accurate canonical Helmholtz free energy model or the solid phase. This approach is similar to that suggested previously by Mehta and Kofke[14] except they proposed using a Helmholtz free-energy density model rather than a *canonical* Helmholtz free-energy model. Note that the difference between these two approaches concerns finite-size effects. Also, they provided results for gas-liquid equilibrium only whereas we calculate three-phase equilibrium at the triple-point of the shifted-force fcc Lennard-Jones system[15]. That is, we use the Gibbs ensemble to simulate liquid-gas, liquid-solid and gas-solid phase coexistence where each gas, liquid and solid phase is identical (within statistical errors) and the solid phase is perfect, i.e. has no defects.

A (NVT) Gibbs ensemble average for a pure system is written[1]

$$A_1(N,V) = \Phi(N,V)^{-1} \sum_{N_1=0}^{N} \int_0^V dV_1 \exp(-\beta(F(N_1,V_1) + F(N_2,V_2)))A(N_1,V_1) \qquad (1)$$

where $\beta = 1 / k_B T$ is the inverse temperature, $N_2 = N - N_1$, $V_2 = V - V_1$, $F(N,V)$ is the canonical Helmholtz free-energy for N particles in volume V

$$F(N,V) = -k_B T \ln\left(\Lambda^{-3N} \int_V \frac{d\mathbf{r}^N}{N!} \exp\left(-\beta H(\mathbf{r}^N)\right)\right) = -k_B T \ln(\Lambda^{-3N} Z(N,V)) \qquad (2)$$

where $\mathbf{r}^N$ indicates the positional and orientational degrees of freedom for N particles, $A(N,V)$ is a canonical ensemble average

$$A(N,V) = Z^{-1}(N,V)\int_V \frac{d\mathbf{r}^N}{N!} A(\mathbf{r}^N)\exp\left(-\beta H(\mathbf{r}^N)\right) \qquad (3)$$

where H is the system's configurational Hamiltonian, and Λ, the thermal de Broglie wavelength, is an irrelevant constant in this study. The partition sum

$$\Phi(N,V) = \sum_{N_1=0}^{N} \int_0^V dV_1 \exp(-\beta(F(N_1,V_1) + F(N_2,V_2))) \qquad (4)$$

normalises the probability of occurrence for each micro-state.

We suggest that for the solid phase $F(N,V)$ and $A(N,V)$ could be calculated *a priori* for each relevant canonical ensemble, i.e. each N, and the Gibbs ensemble average written

$$A_x(N,V) = \Phi(N,V)^{-1} \sum_{N_f=0}^{N} \int_0^V dV_f \exp(-\beta F_s(N_s,V_s)) \int_{V_f} \frac{d\mathbf{r}^{N_f}}{N_f!} \exp\left(-\beta H(\mathbf{r}^{N_f})\right) A(N_x,V_x) \qquad (5)$$

where x can be either solid (subscript *s*) or fluid (subscript *f*). The Gibbs ensemble simulation then proceeds by random intra-box displacements of fluid particles, random insertion and deletion moves in the fluid phase box (that are equivalent to inter-box transfers in a conventional Gibbs simulation) and random volume exchange moves. Intra-box moves are chosen and accepted as per the usual selection rules[1]. If volume exchange moves are chosen so that an amount of volume is transferred from one box to the other at random with uniform probability on the range $-V_{\max}$ to $+V_{\max}$ then they are accepted with probability[1]

$$\min\left\{1, \exp\left(-\beta\Delta F_s - \beta\Delta H_f + N_f \log((V_f + \Delta V)/V_f)\right)\right\} \qquad (6)$$

where ΔV is the change in volume of the fluid box and

$$\begin{aligned} \Delta F_s &= F_s(N_s, V_s - \Delta V) - F_s(N_s, V_s) \qquad (7) \\ \Delta H_f &= H_f(\mathbf{r}^{N_f}(V_f + \Delta V)) - H_f(\mathbf{r}^{N_f}(V_f)) \end{aligned}$$

where the particle centre-of-mass position coordinates are assumed to scale linearly with volume in the usual way. Fluid-phase particles are inserted and deleted according to the acceptance rule

$$\min\left\{1, \exp\left(-\beta\Delta F_s - \beta\Delta H_f + \Delta N \log(V_f) - \log((N_f + \Delta N)!/N_f!)\right)\right\} \qquad (8)$$

where ΔN is the change in the number of particles in the fluid phase and

$$\begin{aligned} \Delta F_s &= F_s(N_s - \Delta N, V_s) - F_s(N_s, V_s) \qquad (9) \\ \Delta H_f &= H_f(\mathbf{r}^{N_f + \Delta N}) - H_f(\mathbf{r}^{N_f}) \end{aligned}$$

Clearly, if at equilibrium $\beta\Delta F_s + \beta\Delta H_f$ is rarely sufficiently small then particle insertions or deletions in the fluid phase box will be unlikely and the method will fail. This is the case for pure hard-spheres where the chemical potential at solid-fluid equilibrium is large and positive (estimated from results in reference [16] and any equation of state for the hard-sphere fluid). It is conceivable that a cavity bias[17] or staged insertion[18] method might lead to useful insertion/deletion acceptance rates for this system. However, for the (shifted-force) Lennard-Jones system at its triple-point the chemical potential is negative and so particle insertions and deletions should be accepted at a useful rate.

The method of Mehta and Kofke replaces $F_s(N,V)$ in (5) with $f_s(N/V)V$, where f_s is the Helmholtz free-energy density of the solid phase. However, both methods converge to the exact result in the thermodynamic limit. Away from this limit these methods will yield different results since they predict different pressures and chemical potentials for the same N and V. To leading order the difference in the chemical potential predicted by these methods can be shown to be[19]

$$\Delta\mu^{ex} = \frac{1}{2N}\left(\frac{\partial P}{\partial \rho}\right)\left(1 - \beta^{-1}\left(\frac{\partial \rho}{\partial P}\right) - \beta^{-1}\rho\left(\frac{\partial^2 P/\partial \rho^2}{(\partial P/\partial \rho)^2}\right)\right) \qquad (10)$$

This difference increases with the inverse of the compressibility and so will be more pronounced for simulations where a solid phase, rather than a gas phase, is represented by a free-energy model. Since in their work Mehta and Kofke employed a free-energy density model for the gas phase this difference could be insignificant. In this work we employ free-energy models for the solid phase and so the difference might be significant for relatively small N.

Calculating the canonical Helmholtz free-energy model

Our Gibbs ensemble method requires $F(N,V)$ and $A(N,V)$ to be calculated for each relevant canonical ensemble of the solid phase. Since in molecular simulations we are forced to set periodic boundaries according to the simulation box shape, the required canonical ensembles with fixed V cannot be simulated directly whilst maintaining perfect crystal structure using the usual periodic boundary scheme. However, an approximate method for calculating the canonical Helmholtz free-energy of each required state of a pure system is as follows. By making use of the extensive approximation

$$A_{ex}(N,V) \approx A_{ex}(N_c, V\frac{N_c}{N})\frac{N}{N_c} \qquad (11)$$

for extensive quantities A_{ex}, and the intensive approximation

$$A_{in}(N,V) \approx A\ \ (N_c, V\frac{N_c}{N}) \qquad (12)$$

for intensive quantities A_{in}, every (N,V) state can be related to another state with a fixed number of particles, N_c, in a volume $V N_c / N$. This approximation becomes exact in the thermodynamic limit. Away from this limit these approximations introduce finite-size errors because they pertain to the canonical ensemble and because of periodic boundary conditions. For intensive quantities, such as the chemical potential, the leading order correction to (12) is of order $(1/N)$ (see equation (10) for example). That is, to reduce finite-size errors (12) should be replaced by

$$A_{in}(N,V) \approx A_{in}(N_c, V\frac{N_c}{N}) + A_{in}^0(N/V)(N^{-1} - N_c^{-1}) \qquad (13)$$

In general A_{in}^0 is different for each density, $\rho = N/V$, and can be found by obtaining A_{in} for two or more values of N at the same density. But for small variations of N from N_c these corrections are also small. In this work we neglect such corrections on this basis.

In the case of a solid phase N_c can be made equal to mN_0 where m is the number of unit cells and N_0 is the number of particles per unit cell. In this work we make use of the probability distribution for states with volume in the infinitesimal range $\{V, V + dV\}$ in an N-particle NPT simulation[1]

$$p(V, V + dV) = \exp\left(-\beta\left(F(V) - PV + \mu N\right)\right)dV \qquad (14)$$

where μ is the chemical potential. This states that if the chemical potential corresponding to the imposed pressure is known then $F(N,V)$ can be calculated absolutely from the volume probability distribution of an NPT simulation. Of course, the problem is that the chemical potential of a crystalline solid corresponding to a pressure P close to coexistence is generally not known in advance for an arbitrary system, and its calculation via thermodynamic integration is lengthy. We will discuss this problem in more detail later.

The triple-point of the shifted-force Lennard-Jones fluid

We test the above method on the shifted force Lennard-Jones system because; 1) it is a simple, well-known model, 2) the chemical potential at the triple-point is known and is negative, 3) we can avoid any potential inaccuracy arising from long-range interactions, and 4) reference results have already been calculated[15]. The shifted-force potential is given by

$$\phi_{sf}(r) = \phi_{LJ}(r) - \phi_{LJ}(r_c) - (r - r_c)\left.\frac{\partial \phi_{LJ}}{\partial r}\right|_{r_c} \qquad (15)$$

where the full LJ potential is

$$\phi_{LJ}(r) = 4\varepsilon\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right) \qquad (16)$$

and ε and σ are the energy and length-scale parameters respectively.

We choose the triple-point temperature determined by Errington et. al.[15], $T^* = k_B T / \varepsilon$ = 0.56, and perform a liquid-gas Gibbs ensemble simulation, noting the density, pressure and chemical potential of each phase. Pressure is calculated from the virial relation[1] while the accurate method of Smit and Frenkel[20] is used to calculate the chemical potential. We then perform a solid-phase fcc crystal NPT simulation at the resulting gas-phase pressure.

The canonical Helmholtz free-energy model is generated by re-arranging (14), choosing a suitably small interval of volume, $dV = 0.2\ \sigma^3$, and using (11). We fit a cubic curve to our data. The results of this NPT simulation and the fitted canonical Helmholtz free-energy model are shown in Figure 1. Also shown is the (canonical) variation of pressure with density calculated using two different routes, i.e. the virial relation and the differential of $-F$ with respect to V. Good agreement is obtained. This free-energy model is then used in the gas-solid and liquid-solid Gibbs ensemble simulations that are performed according to the selection rules in (6) to (9).

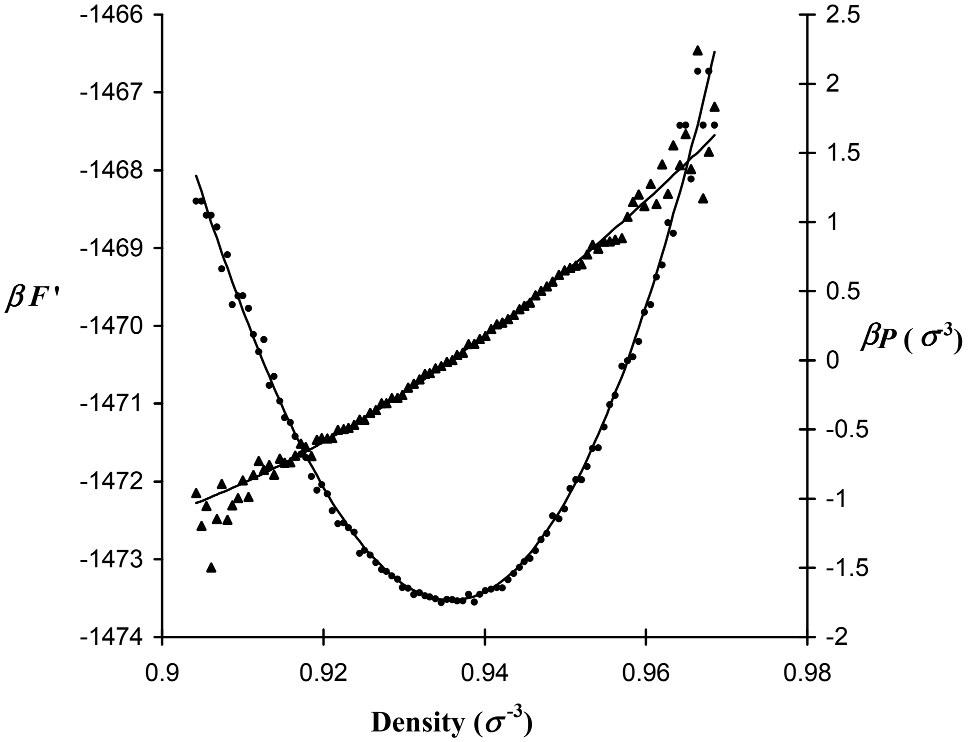

Figure 1. Results of the fcc solid-phase NPT simulation for a shifted-force Lennard-Jones system at $P = 0.00182\varepsilon/\sigma^3$ and $\beta\varepsilon = 0.56$. The circles are Monte-Carlo results for the configurational canonical Helmholtz free-energy ($F' = F - \beta^{-1}N\ln(\Lambda^3)$) and the corresponding line is the cubic polynomial fit, i.e. the model. The triangles show the pressure calculated via the virial relation while the corresponding line is the same calculated by differentiating the canonical Helmholtz free-energy model (with respect to $-V$).

The results in Table 1 show good agreement with the reference results[15] and good consistency with each other. The number of particles in the solid phase of each fluid-solid Gibbs ensemble simulation rarely deviates by more than 100 from its initial value of 256. When combined with (10), where the first and second differentials of pressure with respect to density are estimated from the solid phase NPT simulation (see Figure 1), we obtain an estimate for the error in $\beta\Delta\mu^{ex}$ of about 0.02. This is about the same size as the statistical error in our calculation of the chemical potential at gas-liquid coexistence from the gas-liquid Gibbs ensemble simulation (see Table 1). So we consider the variations in N to be sufficiently small that (11) and (12) are valid, at least for our canonical Helmholtz free-energy model. Of course, the first and second differentials of the pressure with respect to density in (10) refer to the infinite-size system, but our canonical estimates based on the NPT simulation of the solid phase should be sufficiently accurate to *estimate* the magnitude of finite-size effects. The large errors corresponding to the liquid-solid Gibbs simulation result from large and slow fluctuations in the liquid-solid simulation. So this type of simulation must be performed for a sufficiently large number of trial moves.

Discussion

We have shown that fluid-solid equilibrium can be simulated in the Gibbs ensemble provided an accurate canonical Helmholtz free-energy model of the solid phase can be generated. If the chemical potential of the solid phase corresponding to a given pressure is known, or can be easily calculated, then this model is easily generated (with accuracy dependent on finite-size effects only) for defect-free solids by a single NPT simulation. For greater accuracy two or more NPT simulations can be used to generate leading order contributions to finite-size corrections. In principle our approach can also be used for more complex systems such as interaction-site models of alkanes, water and so on in confined geometries. However, approximations (11) and (12) are useful only for pure systems. Further modifications are also necessary if crystals with defects are to be simulated.

Clearly, it is important to be able to efficiently calculate the chemical potential of solid phases. Unfortunately, current methods for calculating the chemical potential of crystalline solids are cumbersome. We soon hope to present a new, efficient and direct method for calculating the chemical potential of crystalline solids. This calculates the difference in Gibbs free energy between one system and another system that is larger by an integral number of crystal unit cells. This is achieved in what we call a ‘dual-ensemble’ by allowing MC moves that switch between these systems and by making use of non-Boltzmann sampling. Further, we hope to extend Tilwani’s[21] ingenious retiling algorithm to arbitrary 3D crystals and apply it to the dual-ensemble to minimise this difference in system size (to 1 crystal unit cell for bulk crystals). This would then provide an efficient and direct method for measuring the free energy and chemical potential of crystalline solids.

Table 1. Results of the gas-liquid (GL), gas-solid (GS) and liquid-solid (LS) Gibbs ensemble simulations of this work and the results in reference 15 for the properties of each phase at the triple-point ($\beta\varepsilon$ = 0.56) of a shifted-force Lennard-Jones model system. The bracketed number at the end of each result for density, pressure and chemical potential is the error to 1 s.d., while the bracketed number at the end of each entry for ‘# Moves’ is the number of rejected trial moves at the start of each simulation. $\mu' = \mu - \beta^{-1}\ln(\Lambda^3)$ is the configurational chemical potential.

Phase	Density (σ^{-3})	P / ε (σ^{-3})	μ' / ε	# Moves
Gas (GL)	0.00336(9)	0.00182(6)	-3.23(2)	390(5)
Liquid (GL)	0.8152(5)	0.001(2)	-3.21(2)	390(5)
Gas (GS)	0.00342(5)	0.00184(2)	-3.22(1)	4(1)
Solid (GS)	0.9362(5)			4(1)
Liquid (LS)	0.810(7)	-0.05(9)	-3.25(7)	495(5)
Solid (LS)	0.933(8)			495(5)
Gas[15]	0.00334	0.0018		
Liquid[15]	0.815			
Solid[15]	0.936			

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