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Simulating Fluid–Solid Equilibrium with the Gibbs Ensemble

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The Gibbs ensemble is employed to simulate fluid–solid equilibrium for a shifted-force Lennard-Jones system. This is achieved by generating an accurate *canonical* Helmholtz free-energy model of the (defect-free) solid phase. This free-energy model is easily generated, with accuracy limited only by finite-size effects, by a single isothermal–isobaric simulation at a pressure not too far from coexistence for which the chemical potential is known. We choose to illustrate this method at the known triple-point because the chemical potential is easily calculated from the coexisting gas. Alternatively, our methods can be used to locate fluid–solid coexistence and the triple-point of pure systems if the chemical potential of the solid phase can be efficiently calculated at a pressure not too far from the actual coexistence pressure. Efficient calculation of the chemical potential of solids would also enable the Gibbs ensemble simulation of bulk solid–solid equilibrium and the grand-canonical ensemble simulation of bulk solids.

Keywords: Gibbs ensemble; Grand-canonical ensemble; Solid–fluid; Solid–solid; Triple point

INTRODUCTION

The Gibbs ensemble is a convenient Monte-Carlo method for simulating phase coexistence. In its original form [1–5] it allows the number of particles and volume in each of two distinct simulation boxes to fluctuate such that the total number and volume is fixed. 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. It has been used to establish coexistence conditions for bulk liquid–gas

phase transitions [1–4] as well as for confined fluid phase transitions such as capillary condensation [6]. Unfortunately, this method can fail if one or both of the coexisting phases is either very dense or solid since then particle transfers between boxes are either very unlikely or undesirable. In the case of dense phases they are unlikely because voids of sufficient size to contain a particle rarely occur at equilibrium. For solids they are undesirable because they generally lead to defects. For these systems the usual method [5] for establishing conditions for phase coexistence relies on creating free-energy density models for each phase and then computing states for which the pressure and chemical potentials in each phase are identical. This can be a laborious process if thermodynamic integration is employed to generate the free-energy models. Alternatively, a much larger system that also incorporates a phase interface can be simulated [7,8].

This work shows that where one or more of the coexisting phases is very dense or solid phase coexistence can be simulated in the Gibbs ensemble provided that accurate *canonical* Helmholtz free-energy models of the troublesome phases can be generated. This approach is similar to that suggested previously by Mehta and Kofke [9] 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. We demonstrate an efficient method for generating these canonical Helmholtz free-energy models whenever the chemical potential

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corresponding to a pressure not too far from coexistence is known.

We apply this approach at the triple-point of the shifted-force Lennard-Jones system [10]. 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. At the triple point the defect-free canonical Helmholtz free-energy model of the face-centered-cubic (fcc) solid phase is easy to generate using a single isothermal–isobaric (NPT) simulation, with accuracy limited only by finite-size effects, since the chemical potential is easily calculated from the coexisting gas. However, in principle the method described below can be used at any temperature to predict fluid–solid coexistence (including the location of the triple-point) provided the chemical potential at a pressure not too far from coexistence can be calculated for the solid phase.

Results for the shifted-force Lennard-Jones system are presented below after first describing our methods.

THEORY

A (NVT) Gibbs ensemble average for a pure system is written [1–5]

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

where $N_2 = N - N_1$, $V_2 = V - V_1$, $F(N, V)$ is the canonical Helmholtz free-energy for N particles in volume V

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

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

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

where H is the system's configurational Hamiltonian, β is the inverse temperature ($1/k_B T$ where k_B is Boltzmann's constant), and Q , the momentum partition function for particle, is an irrelevant constant in this study. The partition sum

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

normalises the probability of occurrence for each micro-state.

This work suggests that where particle transfers between simulation boxes are either unlikely or undesirable because one or more of the phases is either very dense or crystalline then ensemble averages can still be calculated provided $F(N, V)$ and $A(N, V)$ are known *a priori* for each relevant canonical ensemble of each troublesome phase. If solid–fluid coexistence is to be simulated then $F(N, V)$ and $A(N, V)$ could be calculated for the solid phase and the Gibbs ensemble average written

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

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) and random volume exchange moves. Intra-box moves are chosen and accepted as per the usual selection rules [1–5]. 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

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

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

$$\Delta F_s = F_s(N_s, V_s - \Delta V) - F_s(N_s, V_s) \quad (7)$$

$$\Delta H_f = H_f(\mathbf{r}^{N_f}(V_f + \Delta V)) - H_f(\mathbf{r}^{N_f}(V_f))$$

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

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

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

$$\Delta F_s = F_s(N_s - \Delta N, V_s) - F_s(N_s, V_s) \quad (9)$$

$$\Delta H_f = H_f(\mathbf{r}^{N_f + \Delta N}) - H_f(\mathbf{r}^{N_f})$$

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 Ref. [11] and any equation of state for the hard-sphere fluid). It is conceivable that a cavity bias [12] or staged insertion [13] method might lead to useful insertion/deletion acceptance rates for this system. If it does not then an alternative is to generate either canonical Helmholtz free-energy or free-energy density models of both solid and fluid phases. The latter is the usual method [5] for calculating phase coexistence between solid and fluid phases. The former, using the method described below and the Gibbs ensemble, could be more efficient. Another alternative is to use an umbrella sampling [14,15] or phase switch [16,17] method that transforms one phase into the other at constant pressure. However, for the (shifted-force) Lennard-Jones system [10] 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 [9] would replace $F_s(N,V)$ in Eq. (5) with $f_s(N/V)V$, where f_s is a Helmholtz free-energy density. Our approach corresponds to a realizable ensemble whereas that of Mehta and Kofke does not. However, in principle 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 excess chemical potential predicted by these methods can be shown to be [18]

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

This difference increases with the inverse of the compressibility and so will be more pronounced for simulations of solid–fluid than liquid–gas equilibria. 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 . Also, in their work [9] it is not clear how f_s should be generated for a solid phase, particularly for molecular solids. The popular thermodynamic integration scheme with finite-size corrections [5,19,20], initiated from an Einstein crystal, is laborious and complex for molecular solids. A density functional theory approach could be employed for simple systems [21,22], but it is not

clear that this would be accurate or feasible for the general case of molecular solids. Our method generates the canonical Helmholtz free-energy model from a single isothermal–isobaric simulation and is applicable to any pure molecular system.

Our Gibbs ensemble method requires $F(N,V)$ and $A(N,V)$ to be calculated for each relevant canonical ensemble of each troublesome phase. For disordered systems such as liquids an exact but laborious route to $F(N,V)$ and $A(N,V)$ is often available that does not rely on trial insertions or deletions. This consists of using thermodynamic integration for each N , i.e. using [5]

$$F(N, V_1) = F(N, V_0) - \int_{V_0}^{V_1} dV' P(N, V') \quad (11)$$

at constant T and

$$F(N, T_1) = F(N, T_0) \frac{T_1}{T_0} - T_1 \int_{T_0^{-1}}^{T_1^{-1}} \frac{dT'}{T'^2} E(N, T') \quad (12)$$

at constant V , avoiding any phase transition, to obtain $F(N,V)$ and $A(N,V)$ for a given N and a range of V , where the pressure, P , is calculated using the virial relation [5] and E is the total energy. However, a more efficient approximate method, that becomes exact in the thermodynamic limit for pure (single component) systems, is described below.

The problem presented by perfect solid crystals is more complicated. Since in molecular simulations we are forced to set periodic boundaries according to the simulation box shape, the required canonical ensembles with given V cannot generally be simulated directly whilst maintaining perfect crystal structure using the usual periodic boundary scheme. Instead, we make the approximations below.

CALCULATION OF CANONICAL HELMHOLTZ FREE-ENERGIES

An efficient but 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

$$A_{\text{ex}}(N, V) \approx A_{\text{ex}} \left(N_c, V \frac{N_c}{N} \right) \frac{N}{N_c} \quad (13)$$

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

$$A_{\text{in}}(N, V) \approx A \left(N_c, V \frac{N_c}{N} \right) \quad (14)$$

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 Eq. (14) is of order $(1/N)$ (see Eq. (10) for example). That is, to reduce finite-size errors, Eq. (14) should be replaced by

$$A_{\text{in}}(N, V) \approx A_{\text{in}}\left(N_c, V \frac{N_c}{N}\right) + A_{\text{in}}^0(N/V)(N^{-1} - N_c^{-1}) \quad (15)$$

In general A_{in}^0 is different for each A_{in} and each density, 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. By making use of Eqs. (11), (13) and (14) both $F(N, V)$ and $A(N, V)$ for any reasonable N and V can be determined from a single NPT simulation provided $F(N_c, V)$ is known *a priori* for a single given volume, $V = V_0$. For solid phases the use of a single NPT simulation limits the method to perfect crystals. Often in the literature $F(N_c, V_0)$ is calculated using thermodynamic integration [5,19,20]. However, this can be a laborious process and much effort is “wasted” on simulating systems of little interest other than their relevance to the thermodynamic integration process. Instead, 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 [5]

$$p(V, V + dV) = \exp(-\beta(F(V) - PV + \mu N))dV \quad (16)$$

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, at the triple-point the chemical potential is known to be exactly equal to that of the coexisting liquid and gas. So at the triple-point $F(N, V)$ can be constructed from a single NPT simulation with relative ease. Of course, the problem is that fluid–solid coexistence is generally not known in advance for an arbitrary system. However, if the chemical potential corresponding to a given pressure for the solid phase can be calculated then our methods could be used to locate fluid–solid coexistence. To be clear, suppose that a canonical Helmholtz free-energy model is generated at a given temperature by performing an NPT simulation of the solid phase at a particular pressure for which the chemical potential is known or easily calculated and

by using Eq. (16). Then, fluid–solid Gibbs ensemble simulations can be employed to determine whether or not phase coexistence occurs. The pressure at which the chemical potential is known or calculated should be sufficiently close to the coexistence pressure so that the densities sampled by the NPT simulation are close to those sampled by the solid phase at coexistence in the Gibbs simulation.

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 expected to be negative, (3) we can avoid any potential inaccuracy arising from long-range interactions and (4) reference results have already been calculated [10].

The shifted-force potential is given by

$$\phi_{\text{sf}}(r) = \begin{cases} \phi_{\text{LJ}}(r) - \phi_{\text{LJ}}(r_c) - (r - r_c) \frac{\partial \phi_{\text{LJ}}}{\partial r} \Big|_{r_c}; & r \leq r_c \\ = 0 & ; r > r_c \end{cases} \quad (17)$$

where the full LJ potential is

$$\phi_{\text{LJ}}(r) = 4\varepsilon \left(\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right) \quad (18)$$

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

To recap, our method is as follows. We choose the triple-point temperature determined by Errington *et al.*, [10] and perform a liquid–gas Gibbs ensemble simulation, noting the density, pressure and chemical potential of each phase. We choose to initiate this simulation with 108 gas particles and 256 liquid particles at densities equal to the expected equilibrium densities. Pressure is calculated from the virial relation [5] while the accurate method of Smit and Frenkel [23] is used to calculate the chemical potential. We then perform a solid-phase fcc crystal NPT simulation at the resulting gas-phase pressure. We choose to simulate 256 particles and attempt a total of 150 million moves. The canonical Helmholtz free-energy model is generated by re-arranging Eq. (16), choosing a suitably small interval of volume, $dV = 0.2 \sigma^3$, and using Eq. (13). We fit a cubic curve to our data. 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 Eqs. (6)–(9). We choose to use a total of 512 particles for the gas–solid and liquid–solid simulations (with 256 initially in the gas and liquid phases).

The results at the reduced temperature of $T^* = k_B T / \varepsilon = 0.56$ are given in Table I. They show

TABLE I Results of the gas–liquid (GL), gas–solid (GS) and liquid–solid (LS) Gibbs ensemble simulations of this work and the results in reference [10] for the properties of each phase at the triple-point of a shifted-force Lennard-Jones model system. The excess chemical potential, $\mu^{\text{ex}} = \mu + k_{\text{B}}T \ln Q$

Phase	Density (σ^{-3})	Pressure ($\epsilon\sigma^{-3}$)	Excess chemical potential (ϵ)	# Moves (millions)
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 [10]	0.00334	0.0018		
Liquid [10]	0.815			
Solid [10]	0.936			

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.

good agreement with the reference results in [10] 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 Eq. (10), where the first and second differentials of the pressure with respect to density are estimated from the solid phase NPT simulation, we obtain an estimate for the error in $\beta\Delta\mu^{\text{ex}}$ 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 I) So we consider the variations in N to be sufficiently small that Eqs. (13) and (14) are valid, at least for our canonical Helmholtz free-energy model.

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 pressure not too far from coexistence is known, or can be 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. Such corrections will be necessary when the error in $\Delta\mu^{\text{ex}}$ estimated using Eq. (10) is significantly larger than the error in the value of the chemical potential of the solid phase at the chosen pressure.

Since current methods in the literature for calculating the chemical potential are cumbersome we have applied our Gibbs simulation method at a state point for which the chemical potential is easily calculated from the coexisting gas phase at known conditions of pressure and temperature, i.e. at the triple-point. Note that we have not located

the triple-point since we have forced the solid phase model to have the same chemical potential and pressure as the gas phase.

To simulate solid–solid equilibrium in the Gibbs ensemble canonical Helmholtz free-energy models are required for each phase. Each model can be generated in the same way as before, i.e. from one or more NPT simulations of each phase using Eqs. (13)–(16) (provided the chemical potential corresponding to a given pressure is known). The solid–solid Gibbs ensemble simulation can then be performed as for the fluid–solid simulation above (but without any intra-box moves, of course) or the sum over N_1 and the integration over V_1 in Eq. (1) can be performed explicitly.

As with any Gibbs ensemble simulation the fluctuations in the number of particles in each box depends on the relative densities of the coexisting phases. If there is only a small difference in the relative density then fluctuations will be large and so long runs will be required to ensure proper sampling. Our scaling approximations (13) and (14) are more sensitive than usual to this occurrence because they omit finite-size effects. If it is found that coexisting densities are close, resulting in large fluctuations in the number of particles in each box, then two NPT simulations at the same pressure but for different system sizes should be performed and Eq. (15) used so that finite-size effects are incorporated in the canonical Helmholtz free-energy model. This could occur, for example, if solid–solid coexistence is simulated since the relative density difference between the phases is likely to be quite small. In our liquid–solid Gibbs ensemble simulation at the triple point of the Lennard-Jones system the relatively large errors result from large and slow fluctuations in the liquid–solid simulation. Fortunately, they are small enough so that the simple scaling relations (13) and (14) are valid. It is likely that these fluctuations could be “speeded up” if a cavity-biased insertion algorithm is used.

Clearly, it is important to be able to calculate the chemical potential of solid phases with relative ease.

In addition to allowing Gibbs ensemble simulations of fluid–solid equilibrium (and hence allowing the remainder of the fluid–solid phase boundary to be located by thermodynamic integration [24]) it also allows grand-canonical ensemble simulations of the solid phase to be performed at any state point since the canonical Helmholtz free-energy of every relevant state can be determined (with accuracy dependent on finite-size effects only) by Eq. (13). That is, a grand-canonical ensemble average is given by Ref. [5]

$$A(\mu, V) = \Xi(\mu, V)^{-1}$$

$$\times \sum_{N=0}^{\infty} \exp(\beta(\mu N - F(N, V))) A(N, V) \quad (19)$$

where Ξ is the grand-partition sum

$$\Xi(\mu, V) = \sum_{N=0}^{\infty} \exp(\beta(\mu N - F(N, V))) \quad (20)$$

Since each $F(N, V)$ and $A(N, V)$ can be calculated (with accuracy dependent on finite-size effects only) from a single NPT simulation by using Eqs. (13)–(15), each term in Eq. (19) can be calculated without attempting any particle insertions or deletions provided μ in Eq. (16) is known. Unfortunately, current methods in the literature for calculating the chemical potential of solids [19,20] are cumbersome. In future work, we will investigate the possibility of measuring the chemical potential of solids directly by comparing the Gibbs free-energies of two systems, one twice the size of the other, by an extended ensemble, umbrella sampling method that has parallels to the “self-referential” method of Barnes and Kofke [25]. This method might also yield finite-size corrections to the canonical Helmholtz free-energy model automatically.

We have applied our Gibbs ensemble method to a simple system for demonstration, but in principle it can also be used for more complex systems such as interaction-site models of alkanes, water and so on provided the chemical potential of the solid phase can be calculated. It can also be adapted to confined systems such as water in slit-pores [26]. However, approximations (13) and (14) are useful only for pure systems. It is not yet clear whether convenient equivalent methods can be found for mixtures. Further modifications are also necessary if crystals with defects are to be simulated.

References

- [1] Panagiotopoulos, A.Z. (1987) “Direct determination of phase coexistence properties of fluids by Monte-Carlo simulation in a new ensemble”, *Mol. Phys.* **61**, 813.
- [2] Panagiotopoulos, A.Z., Quirke, N., Stapleton, M. and Tildesley, D.J. (1988) “Phase equilibria by simulation in the Gibbs ensemble—alternative derivation, generalization and application to mixture and membrane equilibria”, *Mol. Phys.* **63**, 527.
- [3] Smit, B., de Smedt, P. and Frenkel, D. (1989) “Computer simulations in the Gibbs ensemble”, *Mol. Phys.* **68**, 931.
- [4] Panagiotopoulos, A.Z. (1992) “Direct determination of fluid-phase equilibria by simulation in the Gibbs ensemble—a review”, *Mol. Sim.* **9**, 1.
- [5] Frenkel, D. and Smit, B. (1996) *Understanding Molecular Simulation: From Algorithms to Applications* (Academic Press).
- [6] Panagiotopoulos, A.Z. (1987) “Adsorption and capillary condensation of fluids in cylindrical pores by Monte-Carlo simulation in the Gibbs ensemble”, *Mol. Phys.* **62**, 701.
- [7] For example, see: Gelb, L.D. and Muller, E.A. (2002) “Location of phase equilibria by temperature quench molecular dynamics simulations”, *Fluid Phase Equilib.* **203**, 1.
- [8] For example, see: Chen, B., Siepmann, J.I. and Klein, M.L. (2001) “Direct Gibbs ensemble Monte-Carlo simulations for solid–vapour equilibria: applications to Lennard-Jonesium and carbon-dioxide”, *J. Phys. Chem. B* **105**, 9840.
- [9] Mehta, M. and Kofke, D.A. (1993) “Implementation of the Gibbs ensemble using a thermodynamic model for one of the coexisting phases”, *Mol. Phys.* **79**, 39.
- [10] Errington, J.R., Debenedetti, P.G. and Torquato, S. (2003) “Quantification of order in the Lennard-Jones system”, *J. Chem. Phys.* **118**, 2256.
- [11] Rosenfeld, Y., Schmidt, M., Löwen, H. and Tarazona, P. (1996) “Dimensional crossover and the freezing transition in density functional theory”, *J. Phys. Condens. Matter* **8**, L577.
- [12] Mezei, M. (1987) “Grand-canonical ensemble Monte-Carlo study of dense liquid Lennard-Jones soft-spheres and water”, *Mol. Phys.* **61**, 565.
- [13] For example, see: Kofke, D.A. and Cummings, P.T. (1997) “Quantitative comparison and optimization of methods for evaluating the chemical potential by molecular simulation”, *Mol. Phys.* **92**, 973, and references therein.
- [14] For example, see: Lynden-Bell, R.M., van Duinveldt, J.S. and Frenkel, D. (1993) “Free-energy changes on freezing and melting ductile metals”, *Mol. Phys.* **80**, 801.
- [15] For example, see: Radhakrishnan, R. and Gubbins, K.E. (1999) “Free energy studies of freezing in slit pores: an order-parameter approach using Monte Carlo simulation”, *Mol. Phys.* **96**, 1249.
- [16] Bruce, A.D., Wilding, N.B. and Ackland, G.J. (1997) “Free energy of crystalline solids: a lattice-switch Monte Carlo method”, *Phys. Rev. Lett.* **79**, 3002.
- [17] Wilding, N.B. and Bruce, A.D. (2000) “Freezing by Monte-Carlo phase switch”, *Phys. Rev. Lett.* **85**, 5138.
- [18] Siepmann, J.I., McDonald, I.R. and Frenkel, D. (1992) “Finite-size corrections to the chemical-potential”, *J. Phys. Condens. Matter* **4**, 679.
- [19] Frenkel, D. and Ladd, A.J.C. (1984) “New Monte-Carlo method to compute the free-energy of arbitrary solids—application to the fcc and hcp phases of hard-spheres”, *J. Chem. Phys.* **81**, 3188.
- [20] Chang, J. and Sandler, S.I. (2003) “Determination of liquid–solid transition using histogram reweighting method and expanded ensemble simulations”, *J. Chem. Phys.* **118**, 8390.
- [21] Tarazona, P. (2000) “Density functional for hard-sphere crystals: a fundamental measure approach”, *Phys. Rev. Lett.* **84**, 694. See: for example.
- [22] Cinacchi, G. and Schmid, F. (2002) “Density functional for anisotropic fluids”, *J. Phys. Condens. Matter* **14**, 12223.
- [23] Smit, B. and Frenkel, D. (1989) “Calculation of the chemical-potential in the Gibbs ensemble”, *Mol. Phys.* **68**, 951.
- [24] Kofke, D.A. (1993) “Gibbs-Duhem integration—a new method for direct evaluation of phase coexistence by molecular simulation”, *Mol. Phys.* **78**, 1331.
- [25] Barnes, C.D. and Kofke, D.A. (2002) “Self-referential method for calculation of the free-energy of crystals by Monte Carlo simulation”, *Phys. Rev. E* **65**, 036709.
- [26] Koga, K., Zeng, X.C. and Tanaka, H. (1997) “Freezing of confined water: a bilayer ice phase in hydrophobic nanopores”, *Phys. Rev. Lett.* **79**, 5262.