1 How to calculate the Free Energy

Simulations are very helpful for calculating average values of all observables, including the one of thermodynamic relevance. Still, it is possible to evaluate the free energy by adopting specific strategies.

The simplest strategies is the thermodynamic integration, e.g. the connection via a reversible path, of the required state point with a reference one.

The most common reference point is the ideal gas, which can be accessed as limit for vanishing density or as limit of infinite temperature (for continuous potential only. It is not valid in the case of excluded volume interactions).

Starting from the free energy

$$F(T, V) = U - TS \qquad\qquad dF = dU - TdS - SdT$$

and invoking the first law of thermodynamics $dU = dQ - PdV = TdS - PdV$ one obtain

$$dF = -PdV - SdT$$

The integration of this expression, along V at constant T or along T at constant V provide a mean for evaluating $F(V, T)$.

1.1 From the ideal gas

Aloing an isotherm, $dF = -PdV$ and thus

$$F(V, T) = F(T, V = \infty) - \int_{\infty}^{V} PdV$$

splitting P in the ideal and excess part

$$F(V, T) = F_{idealgas}(T, V) - \int_{\infty}^{V} P^{ex} dV = F_{idealgas}(T, \rho) + N \int_{0}^{\rho} \frac{P_{ex}(\rho, T)}{\rho^2} d\rho$$

or

$$\frac{\beta F(V,T)}{N} = \frac{\beta F_{idealgas}(T,V)}{N} + \frac{1}{k_B T} \int_0^\rho \frac{P_{ex}(\rho,T)}{\rho^2} d\rho$$

1.2 From infinite T

Usually, it is much more convenient not to change the system density. In this case it is possible to integrate along an isochore, where $dQ = dU$ so that

$$dS = \frac{dQ}{T} = \frac{dQ}{dT}\frac{dT}{T} = [C_V^{ig} + C_V^{ex}]\frac{dT}{T}$$

Hence

$$F(V,T) = U(V,T) - TS(V,T) =$$

$$U(V,T) - T\left[S(V,T=\infty) + \int_\infty^T [C_V^{ig}(V,T) + C_V^{ex}(V,T)]\frac{dT}{T}\right] =$$

Joining $S(V,T=\infty)$ with $\int_\infty^T [C_V^{ig}(V,T)\frac{dT}{T}$ to produce the ideal gas entropy at temperature T and splitting U in $U^{ig} + U^{ex}$

$$U^{ex}(V,T) - T\left[-\frac{F^{ig}(V,T)}{T} + \int_\infty^T \frac{dU^{ex}}{dT}\frac{dT}{T}\right]$$

Integrating by part the integral $\int_\infty^T \frac{dU^{ex}}{T}$ and assuming $\frac{U^{ex}(\infty)}{\infty} = 0$,

$$-T\int_\infty^T \frac{dU^{ex}}{T} = -T\left(\frac{U^{ex}(T')}{T'}\right)\Big|_\infty^T + k_B T \int_0^\beta U^{ex}(V,\beta')d\beta'$$

$$= -U^{ex}(V,T) + k_B T \int_0^\beta U^{ex}(V,\beta')d\beta'$$

$$F(V,T) = F^{ig}(V,T) + k_B T \int_0^\beta U^{ex}(V,\beta')d\beta' \tag{1}$$

In the case there is an hard part of the potential, the infinite T limit does not coincide with the ideal gas. In the case the potential is properly hard-sphere

like, the high T limit can be properly modelled with the Carnahan-Starling free energy. In the case of a continuous potential, e.g. the repulsive part of the Lennard-Jones or the soft-sphere potential, the high T limit is not properly defined. A convenient trick can be implemented to calculate the free energy. Indeed one can define a modified potential as

$$V^{modified}(r) = min(V(r), 100k_BT_0)$$

At T_0, the system of particles interacting with $V(r)$ and the one interacting with $V^{modified}(r)$ are identical, since it is extremely rare to sample configurations in which the energy is $100\ k_BT_0$. Hence the free enegy of $V(r)$ and $V^{modified}(r)$ at T_0 coincide. But the modified potential has a clear hight T limit provided by the ideal gas. With a simple change of one line in the MC code, it is possible to run simulations of the modified potential at different T (from T_0 to $T = \infty$ and integrate $\int_0^{\beta_0} U^{ex}(\beta')d\beta'$. This last quantity coincides with $\beta F^{ex}(V, T_0)$. The following figure shows the case of a LJ potential truncated at $r = 3\sigma$ at $\rho\sigma^3 = 0.7$ and $k_BT/\epsilon = 0.7$. In this case $V^{modified}(r) = min(V_{LJ}(r), 100\epsilon)$. Simulations have been run for a system of 256 particles at about 25 different values of β, from $\beta = 10^{-7}$ to $\beta = 1/0.7$. The 25 values have been splined and the spline function has been integrated to evaluate βf^{ex}. The numerical result is $\beta f^{ex}(\rho\sigma^3 = 0.7, T = 0.7) = -4.30$.

Integral = -4.303

LJ ρ=0.7 T=0.7 cutoff=3σ
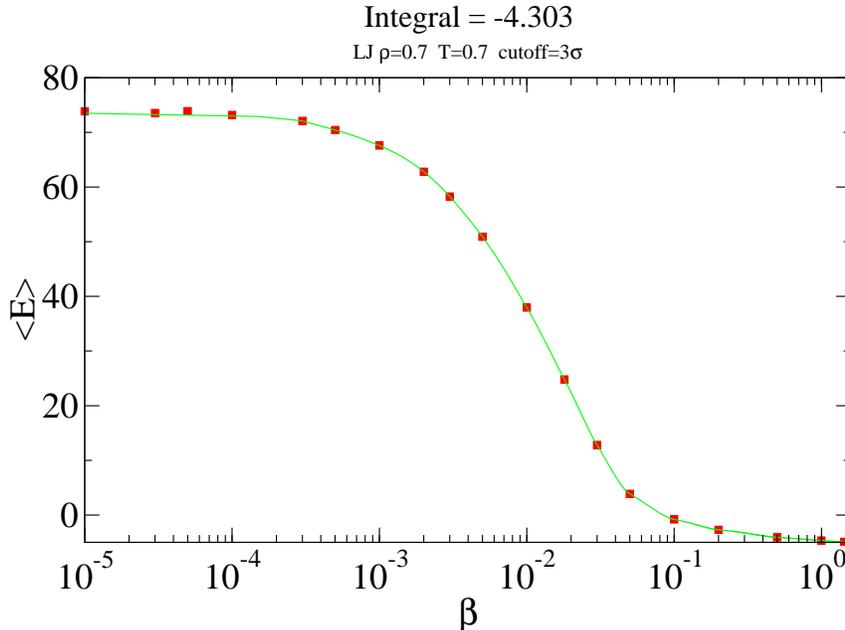
1.3 Integration along the potential shape

A very powerful technique to evaluate differences in Free energy between two related system extent the concept of thermodynamic integration to the case of a path along a sequence of Hamiltonians connecting the starting and ending cases.

Let us assume we know the free energy of a system of N particles interacting with the potential $U(\mathbf{r_1}...\mathbf{r}_N)$ and to be interested in evaluating the free energy of a system of N particles interacting with the potential $U(\mathbf{r_1}...\mathbf{r}_N) + W(\mathbf{r_1}...\mathbf{r}_N)$. We can define intermediate potentials as

$$H_\lambda = U(\mathbf{r_1}...\mathbf{r}_N) + \lambda W(\mathbf{r_1}...\mathbf{r}_N)$$

where λ is a parameter going from zero to one. Then

$$-\beta F_\lambda = \ln Q_\lambda = ln \int e^{-\beta H_\lambda} d\mathbf{r_1}...d\mathbf{r}_N \tag{2}$$

and

$$-\frac{\partial \beta F_\lambda}{\partial \lambda} = \frac{1}{Q_\lambda}\frac{\partial Q_\lambda}{\partial \lambda} = -\frac{1}{Q_\lambda}\int \beta W(\mathbf{r_1}...\mathbf{r}_N)e^{-\beta H_\lambda}d\mathbf{r_1}...d\mathbf{r}_N = -<\beta W>_\lambda$$
$$\tag{3}$$

where $< W >_\lambda$ is the average value of the "perturbation" calculated for a system of N particles interacting with the Hamiltonian H_λ.

The difference in free energy is thus

$$\beta F_1 = \beta F_0 + \int_0^1 <\beta W>_\lambda d\lambda \tag{4}$$

Thus, it is possible to numerically calculate βF_1 starting from the knowledge of βF_0 performing a series of simulations at different λ values and integrating the λ dependence of $< W >_\lambda$.

2   Particle Insertion: Widom Method

A particularly simple and elegant method for measuring the chemical potential μ of a species in a pure fluid or in a mixture is the particle insertion method (often referred to as the Widom method [172]). The statistical mechanics that is the basis for this method is quite simple. Consider the definition of the chemical potential μ_a of a species a. From thermodynamics, we know that μ is defined as

$$\mu_a = \frac{\partial G}{\partial N_a}\Big|_{PTN_{b \neq a}}$$

The partition function of the system (in the NVT ensemble — different relations hold for different ensembles) is

$$Q(N,V,T) = \frac{1}{\Lambda^{3N} N!} \int d\mathbf{r}^N \exp[-\beta \mathcal{U}(\mathbf{r}^N)]$$

For sufficiently large N values,

$$\beta\mu = -\ln \frac{Q(N+1,V,T)}{Q(N,V,T)}$$

so that

$$\beta\mu = -\ln \frac{1}{\Lambda^3(N+1)} \frac{\int d\mathbf{r}^{N+1} \exp[-\beta \mathcal{U}(\mathbf{r}^{N+1})}{\int d\mathbf{r}^N \exp[-\beta \mathcal{U}(\mathbf{r}^N)}$$

By writing $\mathcal{U}(\mathbf{r}^{N+1}) = \mathcal{U}(\mathbf{r}^N) + \Delta \mathcal{U}(\mathbf{r}^N, \mathbf{r}_{N+1})$,

$$\beta\mu = -\ln \frac{1}{\Lambda^3(N+1)} \frac{\int d\mathbf{r}^{N+1} \exp[-\beta \mathcal{U}(\mathbf{r}^N)] \exp[-\beta \Delta \mathcal{U}]}{\int d\mathbf{r}^N \exp[-\beta \mathcal{U}(\mathbf{r}^N)} =$$
$$-\ln \frac{1}{\Lambda^3(N+1)} \int d\mathbf{r}_{N+1} < exp[-\beta \Delta \mathcal{U}] >_N$$

$$= -\ln \frac{V}{\Lambda^3 (N+1)} < exp[-\beta \Delta \mathcal{U}] >_N = \beta \mu_{ig} - \ln < exp[-\beta \Delta \mathcal{U}] >_N$$

where the average denotes canonical ensemble averaging over the configuration space of the N-particle system. The important point to note is that equation (7.2.5) expresses μ_{ex} as an ensemble average that can be sampled by the conventional Metropolis scheme [6]. One aspect of the average in equation (7.2.5) makes it different from the quantities usually sampled in a computer simulation: we have to compute the average of an integral over the position of particle N + 1. This last integral can be sampled by brute force (unweighted) Monte Carlo sampling. In practice the procedure is as follows: we carry out a conventional constant-NVT Monte Carlo simulation on the system of N particles. At frequent intervals during this simulation, we randomly generate a coordinate r_{N+1} uniformly over the volume. For this value of r_{N+1} , we then compute $exp[-\beta \Delta \mathcal{U}]$. By averaging the latter quantity over all generated trial positions, we obtain the average that appears in equation (7.2.5). So, in effect, we are computing the average of the Boltzmann factor associated with the random insertion of an additional particle in an N-particle system, but we never accept any such trial insertions, because then we would no longer be sampling the average needed in equation (7.2.5). The Widom method provides us with a very powerful scheme for computing the chemical potential of (not too dense) atomic and simple molecular liquids.

```
subroutine Widom
xtest=box*ranf()
call ener(xtest,entest)
wrest=wrest
+ +exp(-beta*entest)
return
end
```

Comments to this algorithm:

This algorithm shows the basic structure of the Widom test particle method for the N,V,T ensemble. This subroutine is usually called in the sampling step of a Monte Carlo simulation, for example, in subroutine sample in Algorithm

- 1. Usually, many such test particle insertions are needed to obtain reliable statistics.

- 2. The excess chemical potential follows from $\beta\mu_{ex} = -ln(\sum_i \beta E_i)/M)$, M is the total number of test particle insertions.

- 3. Subroutine ener calculates the energy of the test particle. Note that the test particle insertion is virtual and is never accepted.

- 4. For pairwise additive interactions, we can approximately correct for the effect of the truncation of the intermolecular interactions on the value of the chemical potential by evaluating a tail correction. This correction turns out to be a factor of 2 larger than that for the potential energy per particle (see Case Study 14).

These equations were derived for a spatially homogeneous system. Widorn [173] also considered the case of a spatially inhomogeneous system. In that case, μ_{ex} depends explicitly on the position r. However, in equilibrium the chemical potential itself is constant throughout the system.

In the case in which tail corrections are included, one need to consider the energetic contribution associated to the introduction of the additional particle. The tail correction is

$$U_{N+1}^{tail} - U_N^{tail} = 4\pi(N+1)\frac{N+1}{V}\int_{r_c}^{\infty} r^2 dru(r) - 4\pi N \frac{N}{V}\int_{r_c}^{\infty} r^2 dru(r) =$$

$$4\pi\frac{2N+1}{V}\int_{r_c}^{\infty} r^2 dru(r)$$

We also note that in principle it is possible to derive an equivalent formulation related to the process of extracting a particle. While from a thermodynamic point of view the two formulations are equally valid, from a numerical point of view, the formulation based on the delete of a particle does not converge properly. This is due to the fact that the repulsive part of the potential (that contribute mostly in the delete method) is rarely sampled in the standard MC approach, being irrelevant from a statistical point of view.

2.0.1 Adding o removing ?

In principle, one could also design a Widom-like method by attempting to remove one particle in the system. This method, theoretically correct, provides as expression for the chemical potential

$$\mu = \mu_{ig} + k_B T \ln < e^{+\beta \Delta \mathcal{U}} >$$

One can immediately see that this expression is not going to work for hard-spheres. But even for continuous potential this expression is not really adequate, due to the fact that $\mathcal{U}$ is bounded only from below.

2.1 Overlapping distribution method

A method introduced in the context of a more general technique for measuring free energy differences, first introduced by Bennett [184], is called the overlapping distribution method.

Consider two N-particle systems, labeled 0 and 1 with partition functions Q_0 and Q_1. For convenience we assume that both systems have the same volume V, but this is not essential. From equation (5.4.4) it follows that the free energy difference $\Delta F = F_1 - F_0$ can be written as

$$\beta \Delta F = -\ln \frac{Q_1}{Q_0} = \ln \frac{Q_0}{Q_1}$$

Suppose that we are carrying out a (Metropolis) sampling of the configuration space of system 1. For every configuration visited during this sampling of system 1 we can compute the potential energy of system 0 for the same configuration and, hence, the potential energy difference $\Delta \mathcal{U} = \mathcal{U}_1(\mathbf{r}^N) - \mathcal{U}_0(\mathbf{r}^N)$ We use this information to construct a histogram that measures the probability density for the potential energy difference. Let us denote this probability density by $p_1(\Delta \mathcal{U})$. In the canonical ensemble, $p_1(\Delta \mathcal{U})$ is given by

$$p_1(\Delta\mathcal{U}) = \frac{1}{Q_1} \int d\mathbf{r}^N \exp[-\beta\mathcal{U}_1(\mathbf{r}^N)]\delta(\mathcal{U}_1(\mathbf{r}^N) - \mathcal{U}_0(\mathbf{r}^N) - \Delta\mathcal{U})$$

Due to the presence of the δ-function, the argument of the Boltzmann factor can be changed in

$$p_1(\Delta\mathcal{U}) = \frac{1}{Q_1} \int d\mathbf{r}^N \exp[-\beta(\mathcal{U}_0(\mathbf{r}^N) + \Delta\mathcal{U})]\delta(\mathcal{U}_1(\mathbf{r}^N) - \mathcal{U}_0(\mathbf{r}^N) - \Delta\mathcal{U})$$

$$= \frac{1}{Q_1} \exp[-\beta\Delta\mathcal{U})] \int d\mathbf{r}^N \exp[-\beta\mathcal{U}_0(\mathbf{r}^N)]\delta(\mathcal{U}_1(\mathbf{r}^N) - \mathcal{U}_0(\mathbf{r}^N) - \Delta\mathcal{U})$$

so that

$$p_1(\Delta\mathcal{U}) = \frac{Q_0}{Q_1} \exp[-\beta\Delta\mathcal{U})]p_0(\Delta\mathcal{U})$$

which gives

$$\ln p_1(\Delta\mathcal{U}) = \beta\Delta F - \beta\Delta\mathcal{U}) - \ln p_0(\Delta\mathcal{U})$$

Performing two simulations, one with $\mathcal{U}_1(\mathbf{r}^N)$ and one with $\mathcal{U}_3(\mathbf{r}^N)$, it is possible to estimate $\ln p_1(\Delta\mathcal{U})$ and $\ln p_0(\Delta\mathcal{U})$ as a function of $\Delta\mathcal{U}$. Provided the two functions are properly calculated in a region of overlapping $\Delta\mathcal{U}$ values, it is possible to fit their different and estimate in this way $\beta\Delta F$.

3 Multiple Histograms

As was shown previously the overlapping distribution function method can work even if the two distributions do not really overlap. However, they should not be too far apart. In case there is a large gap between f_0 and f_1, it is often useful to perform additional simulations for intermediate values of the Hamiltonian. We thus obtain a sequence of distribution functions $f_0, f_1, f_2...f_n$, such that f_0 overlaps with f_1, f_1 with f_2 etc. The free energy difference between system 0 and system n can then be obtained by adding $\Delta F = \Delta F_{01} + \Delta F_{12} + \Delta F_{23}...\Delta F_{n-1,n}$. The problem with a naive implementation of this approach is that the statistical errors in the individual free energy differences $\Delta F_{k-1,k}$ add up quadratically in the final result. Fortunately, techniques exist that prevent such error propagation. One approach,

proposed by Ferrenberg and Swendsen [185], is based on the idea that it is possible to construct a self-consistent estimate for the histograms without assuming any specific functional form.

3.0.1 Order Parameter

Let's break for a moment to see how one can properly define a Landau free energy, e.g. an expression of the free energy as a function of an order parameter. This quantity is particularly informative in phase transitions and in several conditions where high free energy barriers separates different configurations (for example in the cis-trans conversion of several molecules) or in the cross-over from different local structures.

The definition of an order parameter is a research field by itself. In the Landau language, it is a quantity that is equal to zero in the disordered phase and different from zero in the ordered one. In addition, the order parameter must reflect the symmetries of the problem. We will possibly touch it again when we will discuss crystallization. You are surely familiar with the Landau free energy for magnetic systems, where the order parameter is identified with the the total magnetization. In the case of fluids, it could be the free energy as a function of the density. When the free-energy as a function of the order parameter shows a non-monotonic behavior, with multiple local minima, a phase transition (or a cross-over between different well defined basins in configuration space) is expected.

If we label the order parameter with the symbol Q, then the probability distribution of sampling Q is

$$P(Q) = \frac{\int e^{-\beta \mathcal{U}} \delta(Q(\mathbf{r}^N) - Q) d\mathbf{r}^N}{\int e^{-\beta \mathcal{U}} d\mathbf{r}^N} \equiv \frac{Z(Q)}{Z}$$

One can thus define a Q dependent free energy

$$\beta F_{landau}(Q) = -\ln P(Q) = -\ln Z(Q) + \ln Z$$

in which the entire Q dependence is in the $Z(Q)$ term. (Note that $\int e^{-\beta F_{landau}(Q)} dQ = 1$)

3.1 Multiple histograms... continue

For what follows, it is convenient to define the distributions that we are considering in a slightly more general form. We assume that the original system that we are studying is characterized by a potential energy function $\mathcal{U}_0$. We now define a sequence of n related models characterized by a potential energy function $\mathcal{U}_i = \mathcal{U}_0 + W_i$ $(i = 1, n)$ For example, W_1 could be $\lambda_1(\mathcal{U}_1 - \mathcal{U}_0)$ with $0 < \lambda_1 < 1$. Alternatively, W_i could be a function of some order parameter or reaction coordinate $Q(\mathbf{r}^N)$. For the sake of generality, we take the latter point of view, because $W_1 = \lambda_1(\mathcal{U}_1 - \mathcal{U}_0)$ can be interpreted as a function of the order parameter $Q \equiv (\mathcal{U}_1 - \mathcal{U}_0)$. We now consider histograms $P_i(Q)$ defined as follows:

$$P_i(Q) = \frac{\int \mathbf{r}^N \exp[-\beta(\mathcal{U}_0 + W_i)]\delta(Q(\mathbf{r}^N) - Q)}{Z_i}$$

where

$$Z_i = \int \mathbf{r}^N \exp[-\beta(\mathcal{U}_0 + W_i)]$$

In some cases, we are interested in the ratio Z_0/Z_n, because that determines the free energy difference between systems 0 and n. But, often, the distribution function $P_0(Q)$ itself is of central interest, because it allows us to compute the Landau free energy of the original system as a function of the order parameter Q:

$$\beta F_{Landau}(Q) = -\ln P_0(Q)$$

3.2 Self-Consistent Histogram Method

In a simulation, the histograms $p_i(Q)$ are estimated by measuring $H_i(Q)$ the number of times that a system with potential energy function $\mathcal{U}_0 + W_i$ has a value on the order of the parameter between Q and $Q + \delta Q$. If the total

number of points collected in histogram i. is denoted by M_i then

$$p_i(Q)\Delta Q = \frac{H_i(Q)}{M_i}$$

If we assume that the "random" variable $H_i(Q)$ (the number of points in the bin i) has a Poisson statistics, then its variance is equal to its average and

$$\frac{<H_i^2(Q)> - <H_i(Q)>^2}{M_i^2} = \frac{<H_i(Q)>}{M_i^2} = \frac{p_i(Q)\Delta Q}{M_i}$$

In what follows, we shall assume, without loss of generality, that our units are chosen such that $\Delta Q = 1$. This choice is not essential, of course, but it simplifies the notation and does not affect the final results. Once we have measured a set of histograms, we can try to combine this information to arrive at an estimate of $p_0(Q)$ or, equivalently, of $F_{Landau}(Q)$. First of all, we should note that, in principle, although not in practice, p_0 can be reconstructed from every individual histogram $p_i(Q)$:

$$p_0(Q) = \exp[+\beta W_i]\frac{Z_i}{Z_0}p_i(Q) \tag{5}$$

In practice, this approach will hardly ever work because the range of Q values where $p_0(Q)$ and $p_i(Q)$ differ significantly from zero need not overlap. Hence the most important contribution to $p_0(Q)$ would come from a range of Q values where $\exp(+\beta W_i)$ is very large but $p_i(Q)$ is vanishingly small. We therefore shall attempt to construct our estimate $p_0^{est}(Q)$ by a linear combination of the estimates based on the different histograms:

$$p_0^{est}(Q) = \sum_i^n w_i(Q) \exp[+\beta W_i(Q)]\frac{Z_i}{Z_0}p_i^{est}(Q) \tag{6}$$

where $w_i(Q)$ is a yet undefined weight function subjected to the constraint

$$\sum_i w_i(Q) = 1$$

Note that, at this stage, the values of the ratios Z_i/Z_0 are also still unknown. Let us now choose the weights $w_i(Q)$ such that the estimated variance in $p_0^{est}(Q)$ is minimised. Using the fact that fluctuations in different simulations are uncorrelated (and hence that the variance of a sum is the sum of all variances e.g. $< p_i p_j > - < p_i >< p_j >= \sigma^2_{p_i} \delta_{ij}$), the variance is

$$< p_0^{est}(Q)^2 > - < p_0^{est}(Q) >^2=$$
$$\sum_i^n w_i(Q)^2 \exp[+2\beta W_i(Q)] \frac{Z_i^2}{Z_0^2} \left(< p_i^{est}(Q)^2 > - < p_i^{est}(Q) >^2 \right)$$

and exploit the previous result

$$< p_0^{est}(Q)^2 > - < p_0^{est}(Q) >^2= \sum_i^n w_i(Q)^2 \exp[+2\beta W_i(Q)] \frac{Z_i^2}{Z_0^2} \frac{p_i(Q)}{M_i}$$

$$= p_0(Q) \sum_i^n w_i(Q)^2 \exp[+\beta W_i(Q)] \frac{Z_i}{Z_0} \frac{1}{M_i}$$

Now we have to minimise the variance with the constraint imposed via a Lagrange multiplier, e.g.

$$\delta(< p_0^{est}(Q)^2 > - < p_0^{est}(Q) >^2 -\alpha \sum_j w_j) = 0$$

which corresponds to

$$p_0(Q) 2 w_i(Q) \delta w_i(Q) \exp[+\beta W_i(Q)] \frac{Z_i}{Z_0} \frac{1}{M_i} - \alpha \delta w_i(Q) = 0$$

This variance is a minimum when

$$w_i(Q) = \frac{\alpha}{2 p_0(Q)} \exp(-\beta W_i(Q)) M_i \frac{Z_0}{Z_i}$$

where α, the Lagrange multiplier, is fixed by the condition that $\sum_j w_j(Q) = 1$, e.g.

$$\alpha = \frac{2p_0(Q)}{\sum \exp(-\beta W_i(Q)) M_i \frac{Z_0}{Z_i}}$$

The best solution for p_0^{est} is thus

$$p_0^{est} = \frac{\sum_i H_i(Q)}{\sum \exp(-\beta W_i) M_i \frac{Z_0}{Z_i}}$$

Going now back to Eq. 5, we can write

$$p_0(Q) \exp[-\beta W_i(Q)] Z_0 = Z_i p_i(Q)$$

and integrating over Q

$$Z_i = \int dQ Z_0 p_0(Q) \exp(-\beta W_i(Q))$$

$$= \int dQ \exp(-\beta W_i(Q)) \frac{\sum_i H_i(Q)}{\sum \exp(-\beta W_i(Q)) \frac{M_i}{Z_i}}$$

This is an implicit equation for Z_i that must be solved self-consistently. In fact, we cannot determine the absolute value of all Z_i but only their ratio. Therefore, we can arbitrarily fix one of the Z_i (e.g. Z_0) at a constant value. The (nonlinear) set of equations is then solved for the remaining Z_i until self-consistency is reached. The free energy difference between system n and system 1 then simply can be computed as

$$\beta \Delta F = -\ln(Z_n / Z_1)$$

To give a specific example, assume that we have simulated only two systems 1 and 2, with potential energy functions $\mathcal{U}_1$ and $\mathcal{U}_1 + \Delta \mathcal{U}$ Moreover, let us assume, for the sake of simplicity, that both simulations resulted in the same number of histogram entries ($M = M_1 = M_2$). Then the previous equation becomes

$$Z_2 = \int d\Delta \mathcal{U} \exp(-\beta \Delta \mathcal{U} \frac{H_1(\Delta \mathcal{U}) + H_2(\Delta \mathcal{U})}{M(1/Z_1 + \exp(-\beta \Delta \mathcal{U})/Z_2)}$$

and dividing everything by Z_1,

$$\frac{Z_2}{Z_1} = \int d\Delta\mathcal{U} \exp(-\beta\Delta\mathcal{U}\frac{H_1(\Delta\mathcal{U}) + H_2(\Delta\mathcal{U})}{M(1 + \exp(-\beta\Delta\mathcal{U})(Z_1/Z_2)}$$

using $\beta\Delta F = -\frac{Z_2}{Z_1}$ we can rewrite the previous equation as

$$\int d\Delta\mathcal{U}\frac{p_1(\Delta\mathcal{U})}{1 + \exp[-\beta(\Delta\mathcal{U} - \Delta F)]} = \int d\Delta\mathcal{U}\frac{p_2(\Delta\mathcal{U})}{1 + \exp[-\beta(\Delta\mathcal{U} - \Delta F)]}$$

which is equivalent to the equation that must be solved self-consistently for ΔF in Bennett's acceptance ratio method [184], to be discussed later on. This is somewhat surprising because the acceptance ratio method was devised to minimize the estimated error in the free energy difference between two systems. In contrast, equation (7.3.10) minimizes the error in our estimate of $p_0(Q)$. If the number of histograms is larger than 2, this expression is not completely equivalent to the one obtained by minimizing the error in the free energy difference between system 1 and n (say). But it is straightforward to derive the equations for the set $\{Z_i\}$ that minimize the error in the estimate of a particular free energy difference.

4   BAR - Bennett acceptance ratio method

The Bennett acceptance ratio method (sometimes abbreviated to BAR) is an algorithm for estimating the difference in free energy between two systems. It was suggested by C. H. Bennett in 1976.[Charles H. Bennett (1976) Efficient estimation of free energy differences from Monte Carlo data. Journal of Computational Physics 22 : 245]

Let's name 0 and 1 the two systems. We can write, multiplying numerator and denominator by the same quantity ($w(\mathbf{r}^N)$ is an arbitrary function of the coordinates)

$$\frac{Q_0}{Q_1} = \frac{Q_0}{Q_1}\frac{\int d\mathbf{r}^N w(\mathbf{r}^N) \exp[-\beta(\mathcal{U}_0 + \mathcal{U}_1)]}{\int d\mathbf{r}^N w(\mathbf{r}^N) \exp[-\beta(\mathcal{U}_0 + \mathcal{U}_1)]} =$$

$$\frac{< w(\mathbf{r}^N) \exp[-\beta(\mathcal{U}_0)] >_1}{< w(\mathbf{r}^N) \exp[-\beta(\mathcal{U}_1)] >_0} \tag{7}$$

which means that the difference in free energy between 0 and 1 can be written as

$$\beta\Delta F = \beta(F_1 - F_0) = \ln\frac{Q_0}{Q_1} = \ln < w(\mathbf{r}^N) \exp[-\beta(\mathcal{U}_0)] >_1 - \ln < w(\mathbf{r}^N) \exp[-\beta(\mathcal{U}_1)] >_0 \tag{8}$$

Bennett focused on the best choice for $w(\mathbf{r}^N)$, e.g. the function that would minimize the numerical error in the evaluation of ΔF.

First of all we need to evaluate the variance of ΔF, $\sigma_{\beta\Delta F}^2$.

To remember of the variance of a function is related to the variance of its argument let's consider

$$y = \ln \xi$$

where $\xi = \frac{\eta}{M}$ and $\eta = \sum_{i=1}^{M} x_i$. Since η is the sum of M random variables, $\sigma_\eta^2 = M\sigma_x^2$ and thus $\sigma_\xi^2 = \frac{\sigma_x^2}{M}$. In addition, since $dy = \frac{d\xi}{\xi}$, $\sigma_y^2 = \frac{\sigma_\xi^2}{\xi^2}$. Putting all this together

$$\sigma_y^2 = \frac{\sigma_\xi^2}{\xi^2} = \frac{\sigma_x^2}{M\xi^2}$$

Applied to $\beta\Delta F$ we then get adding the two variances and defining n_1 and n_2 as the number of sampled configurations in the two simulations

$$\sigma_{\beta\Delta F}^2 = \frac{< (w(\mathbf{r}^N) \exp[-\beta(\mathcal{U}_0)])^2 >_1 - (< w(\mathbf{r}^N) \exp[-\beta(\mathcal{U}_0)] >_1)^2}{n_1(< w(\mathbf{r}^N) \exp[-\beta(\mathcal{U}_0)] >_1)^2} +$$

$$\frac{< (w(\mathbf{r}^N) \exp[-\beta(\mathcal{U}_1)])^2 >_0 - (< w(\mathbf{r}^N) \exp[-\beta(\mathcal{U}_1)] >_0)^2}{n_0(< w(\mathbf{r}^N) \exp[-\beta(\mathcal{U}_1)] >_0)^2}$$

$$= \frac{< (w(\mathbf{r}^N) \exp[-\beta(\mathcal{U}_0)])^2 >_1}{n_1(< w(\mathbf{r}^N) \exp[-\beta(\mathcal{U}_0)] >_1)^2} - \frac{1}{n_1}$$

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$$\frac{< (w(\mathbf{r}^N) \exp[-\beta(\mathcal{U}_1)])^2 >_0}{n_0(< w(\mathbf{r}^N) \exp[-\beta(\mathcal{U}_1)] >_0)^2} - \frac{1}{n_0}$$

Considering that

$$< (w(\mathbf{r}^N) \exp[-\beta(\mathcal{U}_1)])^2 >_0 = \frac{1}{Q_0} \int d\mathbf{r}^N w^2(\mathbf{r}^N) \exp[-2\beta\mathcal{U}_1)] \exp[-\beta\mathcal{U}_0)]$$

and that

$$(< w(\mathbf{r}^N) \exp[-\beta(\mathcal{U}_1)] >_0)^2 = \frac{1}{Q_0^2} \left(\int d\mathbf{r}^N w(\mathbf{r}^N) \exp[-\beta\mathcal{U}_1] \exp[-\beta\mathcal{U}_0] \right)^2$$

one get

$$\sigma^2_{\beta\Delta F} = \frac{Q_0}{n_0} \int d\mathbf{r}^N e^{-\beta\mathcal{U}_1} \left[w^2(\mathbf{r}^N) \exp[-\beta\mathcal{U}_1 - \beta\mathcal{U}_0)] \right] \frac{1}{(d\mathbf{r}^N w(\mathbf{r}^N) \exp[-\beta\mathcal{U}_0 - \beta\mathcal{U}_1])^2} - \frac{1}{n_0} +$$

$$\frac{Q_1}{n_1} \int d\mathbf{r}^N e^{-\beta\mathcal{U}_0} \left[w^2(\mathbf{r}^N) \exp[-\beta\mathcal{U}_1 - \beta\mathcal{U}_0)] \right] \frac{1}{(d\mathbf{r}^N w(\mathbf{r}^N) \exp[-\beta\mathcal{U}_0 - \beta\mathcal{U}_1])^2} - \frac{1}{n_1}$$

The last equation does not change if we multiply w by a constant factor. Without loss of generatity we can this arbitrary constant K by imposing that

$$\int d\mathbf{r}^N w(\mathbf{r}^N) e^{-\beta\mathcal{U}_0 - \beta\mathcal{U}_1} = K$$

(e.g. the denominator of the previous expressions is constant and equal to K)

We can now minimize $\sigma^2_{\beta\Delta F}$ under the constraint $\int d\mathbf{r}^N w(\mathbf{r}^N) e^{-\beta\mathcal{U}_0 - \beta\mathcal{U}_1} = K$ obtaining

$$\delta \left[\sigma^2_{\beta\Delta F} - \lambda \int d\mathbf{r}^N w(\mathbf{r}^N) e^{-\beta\mathcal{U}_0 - \beta\mathcal{U}_1} \right] = 0$$

$$\int d\mathbf{r}^N e^{-\beta \mathcal{U}_0 - \beta \mathcal{U}_1} \left\{ \left(\frac{Q_0}{n_0} e^{-\beta \mathcal{U}_1} + \frac{Q_1}{n_1} e^{-\beta \mathcal{U}_0} \right) \delta \left[\frac{w^2(\mathbf{r}^N)}{K^2} \right] - \lambda \delta w(\mathbf{r}^N) \right\} = 0$$

Substituting $\delta \left[\frac{w^2(\mathbf{r}^N)}{K^2} \right]$ with $2w(\mathbf{r}^N) \delta w(\mathbf{r}^N)/K^2$ the integral vanishes for any arbitrary $\delta w(\mathbf{r}^N)$ if

$$\left\{ \left(\frac{Q_0}{n_0} e^{-\beta \mathcal{U}_1} + \frac{Q_1}{n_1} e^{-\beta \mathcal{U}_0} \right) \frac{2w(\mathbf{r}^N)}{K^2} - \lambda \right\} = 0$$

e.g.

$$w(\mathbf{r}^N) = \frac{constant}{\left(\frac{Q_0}{n_0} e^{-\beta \mathcal{U}_1} + \frac{Q_1}{n_1} e^{-\beta \mathcal{U}_0} \right)}$$

that provides the best $w(\mathbf{r}^N)$.

Substituting this functional form in Eq. 7 the constant disappears and

$$\frac{Q_0}{Q_1} = \frac{< \frac{\exp[-\beta(\mathcal{U}_0)]}{\left(\frac{Q_0}{n_0} e^{-\beta \mathcal{U}_1} + \frac{Q_1}{n_1} e^{-\beta \mathcal{U}_0} \right)} >_1}{< \frac{\exp[-\beta(\mathcal{U}_1)]}{\left(\frac{Q_0}{n_0} e^{-\beta \mathcal{U}_1} + \frac{Q_1}{n_1} e^{-\beta \mathcal{U}_0} \right)} >_0} = \frac{< \frac{1}{\left(\frac{Q_0}{n_0} e^{-\beta \mathcal{U}_1 + \beta \mathcal{U}_0} + \frac{Q_1}{n_1} \right)} >_1}{< \frac{1}{\left(\frac{Q_0}{n_0} + \frac{Q_1}{n_1} e^{-\beta \mathcal{U}_0 + \beta \mathcal{U}_1} \right)} >_0} \tag{9}$$

Now we define

$$\frac{Q_0}{n_0} \frac{n_1}{Q_1} = \exp[\beta C] \tag{10}$$

so that formally Eq. 9 simplifies in

$$\frac{Q_0}{Q_1} = \frac{< \frac{1}{\frac{Q_1}{n_1}(e^{\beta C - \beta \mathcal{U}_1 + \beta \mathcal{U}_0} + 1)} >_1}{< \frac{1}{\frac{Q_0}{n_0}(1 + e^{-\beta C - \beta \mathcal{U}_0 + \beta \mathcal{U}_1})} >_0}$$

$$= \frac{< \left(e^{\beta C - \beta \mathcal{U}_1 + \beta \mathcal{U}_0} + 1 \right)^{-1} >_1}{< \left(1 + e^{-\beta C - \beta \mathcal{U}_0 + \beta \mathcal{U}_1} \right)^{-1} >_0} e^{\beta C}$$

Remembering that the Fermi-Dirac function $f_{FD} \equiv \frac{1}{1+e^x}$ we can write

$$\frac{Q_0}{Q_1} = \frac{< f_{FD}(\beta(\mathcal{U}_0 - \mathcal{U}_1 + C)) >_0}{f_{FD}(\beta(\mathcal{U}_1 - \mathcal{U}_0 - C)) >_1} e^{\beta C} \tag{11}$$

Now... what is C ? C is nothing more than the free energy change (see Eq. 10)

$$\beta C = \beta \Delta F + \ln \frac{n_1}{n_0} \qquad \beta \Delta F = \beta C - \ln \frac{n_1}{n_0}$$

From Eq. 11 one also has

$$\beta \Delta F = \ln \frac{\frac{1}{n_0} \sum_{i=1}^{n_0} f_{FD}(\beta(\mathcal{U}_0 - \mathcal{U}_1 + C))}{\frac{1}{n_1} \sum_{i=1}^{n_1} f_{FD}(\beta(\mathcal{U}_1 - \mathcal{U}_0 - C))} + \beta C$$

The only way both expression are satisfied is that the value of C is the one such that

$$\sum_{i=1}^{n_0} f_{FD}(\beta(\mathcal{U}_0 - \mathcal{U}_1 + C)) = \sum_{i=1}^{n_1} f_{FD}(\beta(\mathcal{U}_1 - \mathcal{U}_0 - C))$$

In practical situations, C is treated as a adjustable parameter that is varied untill the previous equation is satisfied. Once C has been found, the free energy difference is also knon from $\beta \Delta F = \beta C - \ln \frac{n_1}{n_0}$.

5 MBAR, Multistate Bennett acceptance ratio

The multistate Bennett acceptance ratio (MBAR) is a generalization of the Bennett acceptance ratio that calculates the (relative) free energies of several multi states. It essentially reduces to the BAR method when only two super states are involved.

6 Umbrella Sampling

Umbrella sampling is a technique in computational physics and chemistry, used to improve sampling of a system (or different systems) where ergodicity is hindered by the form of the system's energy landscape. It was first suggested by Torrie and Valleau in 1977. It is a particular physical application of the more general importance sampling in statistics.

Umbrella Sampling aims at obtaining an accurate estimate of the free energy difference between two systems (0 and 1), one should sample both the part of configuration space accessible to system 1 and the part accessible to 0.

The method is based on the idea that it is possible to extract information on the umperturbed system also simulating it with a modified hamiltonian. With a proper choice of this modified hamiltonian, free-energy barriers can be flatten out and the system can sample all relevant state point in one single simulation.

To see how the method works, let's consider replacing the Boltzmann factor of the system by a non-negative weight function $\pi(\mathbf{r}^N)$,

$$\pi(\mathbf{r}^N) = \frac{\omega(\mathbf{r}^N)e^{-\beta \mathcal{U}_0}}{\int d\mathbf{r}^N \omega(\mathbf{r}^N)e^{-\beta \mathcal{U}_0}}$$

corresponding to a system with potential energy $\mathcal{U}_0 - k_B T \ln w$.

The expression for the average value of a generic observable $< \mathcal{A} >_0$ is

$$< \mathcal{A} >_0 = \frac{\int \exp(-\beta \mathcal{U}_0)\mathcal{A}(\mathbf{r}^N)d\mathbf{r}^N}{\int \exp(-\beta \mathcal{U}_0)d\mathbf{r}^N}$$

and multiplying by the identity $\pi(\mathbf{r}^N)/\pi(\mathbf{r}^N)$

$$< \mathcal{A} >_0 = \frac{\int \exp(-\beta \mathcal{U}_0)\pi(\mathbf{r}^N)\frac{\mathcal{A}(\mathbf{r}^N)}{\pi(\mathbf{r}^N)}d\mathbf{r}^N}{\int \exp(-\beta \mathcal{U}_0)\pi(\mathbf{r}^N)\frac{1}{\pi(\mathbf{r}^N)}d\mathbf{r}^N}$$

$$< \mathcal{A} >_0 = \frac{\int d\mathbf{r}^N \pi(\mathbf{r}^N) \frac{\mathcal{A}(\mathbf{r}^N)}{w(\mathbf{r}^N)}}{\int d\mathbf{r}^N \pi(\mathbf{r}^N)(\mathbf{r}^N)\frac{1}{w(\mathbf{r}^N)}}$$

or introducing the notation $< ..... >_\pi$ to denote an average over a probability distribution proportional to $\pi(\mathbf{r}^N)$,

$$< \mathcal{A} >_0 = \frac{< \frac{\mathcal{A}(\mathbf{r}^N)}{w(\mathbf{r}^N)} >_\pi}{< \frac{1}{w(\mathbf{r}^N)} >_\pi}$$

Going back to the problem of evaluating the difference in free energy between to states 0 and 1, we have seen that

$$\exp[-\beta \Delta F] = < \exp[-\beta(\mathcal{U}_1 - \mathcal{U}_0)] >_0$$

In the umbrella sampling scheme, identifying $\mathcal{A} \equiv \exp[-\beta(\mathcal{U}_1 - \mathcal{U}_0)]$

$$\exp[-\beta \Delta F] = \frac{< \frac{\exp[-\beta(\mathcal{U}_1 - \mathcal{U}_0)]}{w(\mathbf{r}^N)} >_\pi}{< \frac{\exp[-\beta \mathcal{U}_0]}{\exp[-\beta \mathcal{U}_0]w(\mathbf{r}^N)} >_\pi} = \frac{< \frac{\exp[-\beta \mathcal{U}_1]}{\pi(\mathbf{r}^N)} >_\pi}{< \frac{\exp[-\beta \mathcal{U}_0]}{\pi(\mathbf{r}^N)} >_\pi}$$

For both the numerator and the denominator in this equation to be non-zero, $\pi(\mathbf{r}^N)$ should have an appreciable overlap with both regions of configuration space that are sampled by system 0 and system 1. This bridging property of π is responsible for the name umbrella sampling. At first sight, it might seem advantageous to refine the computation of π in such a way that all relevant configurations can be sampled in one run. Surprisingly, this is not the case. It is usually better to perform several umbrella sampling runs in (partially overlapping) windows. Umbrella sampling is a very general technique and, in principle, will give the correct answer independently of the umbrella potential that is used. However, the efficiency of this method does depend very much on a clever choice of this umbrella potential.

Before concluding, let's consider the case of a double-minima order parameter. If we can provide a good estimate of $P(Q)$ in advance, let's call it $P_{bias}(Q)$, then we could define

$$\pi = \frac{e^{-\ln P_{bias}(Q)} e^{-\beta H_0}}{Z_\pi}$$

so that

$$\beta F_\pi(Q) = -\ln P_\pi(Q) = -\ln \frac{\int e^{-\ln P_{bias}(Q)} e^{-\beta H_0} \delta(Q(\mathbf{r}^N) - Q) d\mathbf{r}^N}{Z_\pi}$$

$$= -\ln P_{bias}^{-1}(Q) \frac{\int e^{-\beta H_0} \delta(Q(\mathbf{r}^N) - Q) d\mathbf{r}^N}{Z_\pi} = \ln P_{bias}(Q) - \ln P_0(Q) - \ln \frac{Z_0}{Z_\pi}$$

that shows that with a proper choice of $P_{bias}(Q)$, the barrier in the order parameter is completely flatten out and the system can sample all relevant Q values with the same statistics.

The method can be applied also to other ensambles. For example in the case of GCMC, US modifies the standard GCMC insertion/removal probabilities as follows:

$$P_{ins}^{US-GCMC} = P_{ins}^{GCMC} \frac{P_{ex}(N)}{P_{ex}(N+1)}$$

and

$$P_{del}^{US-GCMC} = P_{del}^{GCMC} \frac{P_{ex}(N)}{P_{ex}(N-1)}$$

Indeed

$$\pi = \frac{e^{-\ln P_{bias}(N)} e^{-\beta H_0}}{Z_\pi}$$

and so the Boltzman weight of the "new" state is $\frac{e^{-\beta H_0}}{P_{bias}(N_{new})}$

In these last equations $P_{ex}(N)$ is a forecast on the real probability of finding N particles $P(N)$ which can be for example extracted from previous higher-T simulations through the histogram reweighting technique. If the predicted probability distribution $P_{ex}(N)$ is a good approximation to the real $P(N)$, the resulting biased probability will result in being flat in N and the system will thus not experience any difficulty in crossing the barrier between the liquid and gas phase.

7 Phase Coexistence - The Gibbs ensemble method

In many respects, computer simulations resemble experiments. Yet, in the study of first-order phase transitions, there seems to be a difference. In experiments, a first-order phase transition is easy to locate: at the right density and temperature, we will observe that an initially homogeneous system will separate into two distinct phases, divided by an interface. Measurement of the properties of the coexisting phases is then quite straightforward. In contrast, in a simulation we often locate a first-order phase transition by computing the thermodynamic properties of the individual phases, then finding the point where the temperature, pressure, and chemical potential(s) of the two bulk phases are equal. The reason we are usually forced to follow this more indirect route in a simulation is related to the small size of the system studied. If two phases coexist in such systems, a relatively large fraction of all particles resides in or near the interface dividing the phases. To estimate this effect, consider the idealized case that we have a cubic domain of one phase, surrounded by the other. We assume that the outermost particles in the cube belong to the interface and that the rest is bulk-like. The fraction of particles in the interface depends on the system size. Tipicallu, systems with fewer than 1000 particles are interface dominated. And, even for quite large systems, the fraction of particles in the interface is nonnegligible. It is essential therefore to use relatively large systems to calculate reliable coexistence properties. Unfortunately, for large systems long equilibration times are needed, not only because the systems contain many particles, but also because equilibration times in two-phase systems tend to be longer than those in homogeneous systems.

Direct simulations of first-order phase coexistence therefore often are computationally rather expensive) However, in the mid-1980s, Panagiotopoulos [94] devised a new computational scheme for studying first-order phase transitions. This scheme has many of the advantages of a direct simulation of coexistence yet few of its disadvantages. Where applicable, this scheme (usually referred to as the Gibbs ensemble method) results in a very significant reduction of the computer time required for phase equilibrium calculations. With this method, phase equilibria can be studied in a single simulation. At present, the Gibbs ensemble method has become the technique par excellence

to study vapor-liquid and liquid-liquid equilibria. However, like simulations in the grand-canonical ensemble, the method does rely on a reasonable number of successful particle insertions to achieve compositional equilibrium. As a consequence, the Gibbs ensemble method is not very efficient for studying equilibria involving very dense phases. However, there is a technique that greatly facilitates the numerical study of phase equilibria of dense phases. This is the so-called semigrand ensemble method of Kofke and Glandt [198], which is discussed in chap.9 of Frenkel and Smith. The success of the Gibbs ensemble method relies on the possibility of exchanging particles between the two coexisting phases. If one of the coexisting phases is a crystal, one would need to find a vacancy in order to insert a particle. However, the equilibrium concentration of such defects is usually so low that the conventional Gibbs ensemble method becomes impractical. Tilwani and Wu [199] suggested an alternative approach in which an atom is added to the unit box of the solid and this new unit box is used to fill up (tile) space. In this way particles can be added or removed from the system, while the crystal structure is maintained. Tilwani and Wu showed that for the two-dimensional square-well fluid, their method agrees well with the results from free energy calculations [200].

The condition for coexistence of two or more phases I, II,.. is that the pressure of all coexisting phases must be equal ($P_I = P_{II} = P$), as must be the temperature ($T_I = T_{II} = T$) and the chemical potentials of all species ($\mu_I^\alpha = \mu_{II}^\alpha = \mu^\alpha$) Hence, one might be inclined to think that the best ensemble for studying would be the constant μPT ensemble. The quotation marks around the name of this "ensemble" are intentional, because, strictly speaking, no such ensemble exists. The reason is simple: if we specify only intensive parameters, such as P, T and μ the extensive variables (such as V) are unbounded. Another way to say the same thing is that the set P, T, μ is linearly dependent. To get a decent ensemble, we must fix at least one extensive variable. In the case of constant-pressure Monte Carlo simulations this variable is the number of particles N, while in grand-canonical Monte Carlo the volume V of the system is fixed. After this introduction, it may come as a surprise that the Gibbs ensemble method of Panagiotopoulos [94,147] comes very close to achieving the impossible: simulating phase equilibria under conditions where the pressure, temperature, and chemical potential(s) of

the coexisting phases are equal. The reason this method can work is that, although the difference between chemical potentials in different phases is fixed (namely, at $\Delta\mu = 0$), the absolute values are still undetermined. Here, we show how the Gibbs ensemble method can be derived, following the approach developed in the previous chapters.

At this stage, we focus on the version of the Gibbs ensemble where the total number of particles and the total volume of the two boxes remain constant; that is, the total system is at N, V, T conditions. The description of the N, P, T version can be found in [147]. This constant-P method can be applied only to systems containing two or more components because in a one-component system, the two-phase region is a line in the $P - T$ plane. Hence, the probability that any specific choice of P and T will actually be at the phase transition is vanishingly small. In contrast, for two-component systems, the two-phase region corresponds to a finite area in the $P - T$ plane. Note that in either formulation of the Gibbs method, the total number of particles is fixed. The method can be extended to study inhomogeneous systems [146] and is particularly suited to study phase equilibria in multi-component mixtures [147]. A review of applications of the Gibbs ensemble technique is given in [201]. The great advantage of the Gibbs method over the conventional techniques for studying phase coexistence is that, in the Gibbs method, the system spontaneously "finds" the densities and compositions of the coexisting phases. Hence, there is no need to compute the relevant chemical potentials as a function of pressure at a number of different compositions and then construct the coexistence line.

7.1 The Partition Function - Gibbs Ensamble

In his original article [94], Panagiotopoulos introduced the Gibbs ensemble as a combination of the N, V, T ensemble, N, P, T ensemble, and Vt, V, T ensemble. In the previous section we stated that the Gibbs ensemble is not a "constant-μ, P, T ensemble", but we did not say what ensemble it actually corresponds to. This point is considered in detail in Appendix H of Frenkel and Smith, where we demonstrate that, in the thermodynamic limit, the (constant-V) Gibbs ensemble is rigorously equivalent to the canonical

ensemble.

We start our discussion with the expression for the partition function for a system of N particles distributed over two volumes V_1 and $V_2 = V - V_1$, where the particles interact with each other in volume 1 and 2

$$Q(N, V_1, V - V_1, T) = \sum_{n_1=0}^{N} \frac{V_1^{n_1}(V - V_1)^{N-n_1}}{\Lambda^{3N} n_1!(N - n_1)!} \times$$

$$\int d\mathbf{s}_2^{N-n_1} \exp[-\beta U(\mathbf{s}_2^{N-n_1})] \int d\mathbf{s}_1^{n_1} \exp[-\beta U(\mathbf{s}_1^{n_1})]$$

We have now to integrate over the volume V_1 ($\frac{1}{V} \int_0^V dV_1$), which means a partition function

$$Q(N, V, T) = \sum_{n_1=0}^{N} \frac{1}{V \Lambda^{3N} n_1!(N - n_1)!} \times$$

$$\int_0^V dV_1 V_1^{n_1}(V - V_1)^{N-n_1} \int d\mathbf{s}_2^{N-n_1} \exp[-\beta U(\mathbf{s}_2^{N-n_1})] \int d\mathbf{s}_1^{n_1} \exp[-\beta U(\mathbf{s}_1^{n_1})]$$

and a probability to find the system with n_1 particles in V_1 at positions $\mathbf{s}_1^{n_1}$ and $N - n_1$ particles in $V - V_1$ at position $\mathbf{s}_2^{N-n_1}$

$$\mathcal{N}(n_1, V_1, \mathbf{s}_1^{n_1}, \mathbf{s}_2^{N-n_1}) \sim \frac{V_1^{n_1}(V - V_1)^{N-n_1}}{n_1!(N - n_1)!} \exp[-\beta U(\mathbf{s}_2^{N-n_1})] \exp[-\beta U(\mathbf{s}_1^{n_1})] =$$

$$\frac{V_1^{n_1}(V - V_1)^{N-n_1}}{n_1!(N - n_1)!} \exp[-\beta U(\mathbf{s}^N)]$$

This equation suggests the following Monte Carlo scheme for sampling all possible configurations of two systems that can exchange particles and volume. In this scheme, we consider the following trial moves

- 1. Displacement of a randomly selected particle.

- 2. Change of the volume in such a way that the total volume remains constant.

- 3. Transfer of a randomly selected particle from one box to the other.

These moves are shown schematically in the following figure:
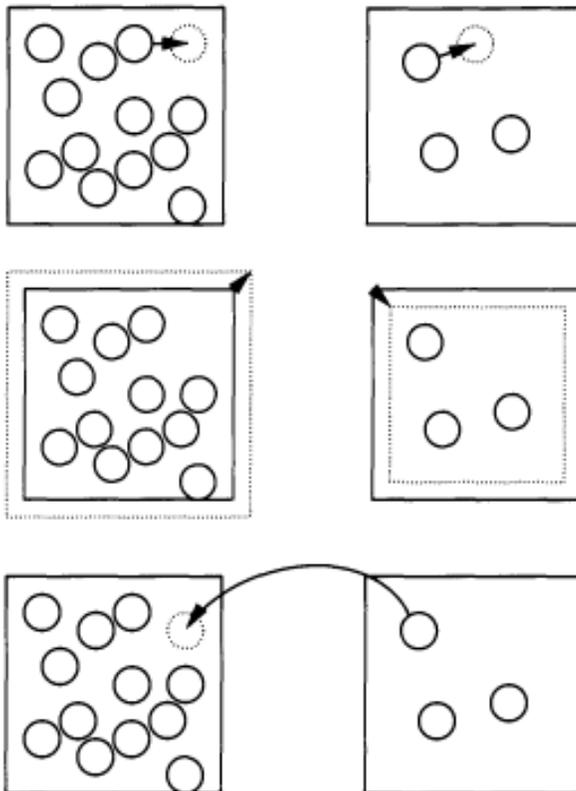
Figure 8.2: Monte Carlo steps in the Gibbs ensemble method: particle displacement, volume change, and exchange of particles.

The acceptance rules for these steps in the Gibbs ensemble can be derived from the condition of detailed balance

$$\mathcal{K}(old \rightarrow new) = \mathcal{K}(new \rightarrow old)$$

where $\mathcal{K}(old \rightarrow new)$ is the flow of configuration old to new, which is equal to the product of the probability of being in configuration old $\mathcal{N}(old)$, the probability of generating configuration new $\alpha(old \rightarrow new)$, and the probability of accepting this move $acc(old \rightarrow new)$:

$$\mathcal{K}(old \rightarrow new) = \mathcal{N}(old) \times \alpha(old \rightarrow new) acc(old \rightarrow new)$$

The MC code is composed of three type of moves: particle displacement, volume exchange and particle exchange. The displacemnt of a randomly selected particle in the same box is performed as usual in standard MC codes, e.g. by accepting with the Boltzmann probability. The acceptance probability for the volume change moves $V_1(new) = V_1(old) + \Delta V$ can be evaluated considering that

$$\frac{\mathcal{N}(new)}{\mathcal{N}(old)} = \frac{V_1(new)^{n_1}(V - V_1(new))^{N-n_1}}{V_1(old)^{n_1}(V - V_1(old))^{N-n_1}} \frac{\exp[-\beta U(\mathbf{s_{new}}^N)]}{exp[-\beta U(\mathbf{s_{old}}^N)]}$$

which suggests

$$\alpha(old \rightarrow new) = min\left\{1, \frac{V_1(new)^{n_1}(V - V_1(new))^{N-n_1}}{V_1(old)^{n_1}(V - V_1(old))^{N-n_1}} \frac{\exp[-\beta U(\mathbf{s_{new}}^N)]}{exp[-\beta U(\mathbf{s_{old}}^N)]}\right\}$$

If we perform a random walk in $\xi = \ln(\frac{V_1}{V-V_1})$, so that the domanin of ξ coincides with all possible V_1 values, (e.g. with $d\xi = \frac{(V-V_1)+V_1}{(V-V_1)^2}\frac{V-V_1}{V_1}dV_1 = \frac{V}{V_1(V-V_1)}dV_1$) then the partition function can be written as

$$Q(N, \xi, T) = \sum_{n_1=0}^{N} \frac{1}{V\Lambda^{3N}n_1!(N-n_1)!} \times$$

$$\int_0^V d\xi \frac{V_1(V-V_1)}{V} V_1^{n_1}(V-V_1)^{N-n_1} \int ds_2^{N-n_1} \exp[-\beta U(s_2^{N-n_1})] \int ds_1^{n_1} \exp[-\beta U(s_1^{n_1})]$$

and

$$\frac{\mathcal{N}(new)}{\mathcal{N}(old)} = \frac{V_1(new)^{n_1+1}(V - V_1(new))^{N-n_1+1}}{V_1(old)^{n_1+1}(V - V_1(old))^{N-n_1+1}} \frac{\exp[-\beta U(\mathbf{s_{new}}^N)]}{\exp[-\beta U(\mathbf{s_{old}}^N)]}$$

and finally

$$\alpha(old \rightarrow new) = min\left\{1, \frac{V_1(new)^{n_1+1}(V - V_1(new))^{N-n_1+1}}{V_1(old)^{n_1+1}(V - V_1(old))^{N-n_1+1}} \frac{\exp[-\beta U(\mathbf{s_{new}}^N)]}{exp[-\beta U(\mathbf{s_{old}}^N)]}\right\}$$

Concerning the particle exchange, if we remove a particle from volume V_1 and insert it in volume $V - V_1$, we have

$$\frac{\mathcal{N}(new)}{\mathcal{N}(old)} = \frac{\frac{V_1^{n_1-1}(V-V_1)^{N-n_1+1}}{(n_1-1)!(N-n_1+1)!}\exp[-\beta U(\mathbf{s_{new}}^N)]}{\frac{V_1^{n_1}(V-V_1)^{N-n_1}}{n_1!(N-n_1)!}\exp[-\beta U(\mathbf{s_{old}}^N)]}$$

$$= \frac{n_1}{(N-n_1+1)}\frac{(V-V_1)}{V_1}\frac{\exp[-\beta U(\mathbf{s_{new}}^N)]}{\exp[-\beta U(\mathbf{s_{old}}^N)]}$$

which suggests a Metropolisi-like acceptance rule for removing a particle from volume V_1 and insert it in volume $V - V_1$

$$\alpha(old \to new) = min\left\{1, \frac{n_1}{(N-n_1+1)}\frac{(V-V_1)}{V_1}\frac{\exp[-\beta U(\mathbf{s_{new}}^N)]}{\exp[-\beta U(\mathbf{s_{old}}^N)]}\right\}$$

7.2 Implementation

A convenient method for generating trial configurations is to perform a simulation in cycles. One cycle consists of (on average) Npart attempts to displace a (randomly selected) particle in one of the (randomly chosen) boxes, Nvol attempts to change the volume of the subsystems, and Nswap attempts to exchange particles between the boxes. It is important to ensure that at each step of the simulation the condition of microscopic reversibility is fulfilled. In the original implementation of a Gibbs ensemble simulation the calculations were performed slightly differently [94]; instead of making a random choice of the type of trial move (particle displacement, volume change, or particle exchange) at every Monte Carlo step, the different trial moves were carried out in a fixed order. First, N attempts were made to move every particle in succession (the N, V, T part), then one attempt was made to change the volume (the N, P, T part), and finally N try attempts were made to exchange particles (the μ, V, T part). However, if in a simulation it is possible to choose from a repertoire of trial moves, random selection of the type of trial move is recommended, because this way microscopic reversibility is guaranteed. An additional disadvantage of performing trial moves in a fixed order is that it may make a difference at what point in the program the measurement of the physical properties is performed (e.g., after the N, V, T part, the N, P, T

part, or the μ, V, T part). If trial moves are selected at random, all trial moves are on average equivalent and one can simply perform measurements after a predetermined number of MC cycles.

```
PROGRAM mc_Gibbs
do icycl=l,ncycl
ran=ranf()*(npart+nvol+nswap)
if (ran.le.npart) then
call mcmove
else if (ran.le.(npart+nvol))
call mcvol
else
call mcswap
endif
call sample
enddo
end
```

```
SUBROUTINE mcvol
call toterg(boxl,enlo)
call toterg(box2,en2o)
vol=boxl**3
vo2=v-vol
lnvn=log (vol/vol2) +
+ (ranf()-0.5)*vmax
vln=v*exp (lnvn) / (l+exp (lnvn))
v2n=v-vln
boxln=vln**(1/3)
box2n=v2n**(1/3)
do i=l,npart
if (ibox(i).eq.1) then
fact=boxln/boxlo
else
fact=box2n/box2o
```

```
endif
x(i)=x(i)*fact
enddo
call toterg(boxln,enln)
call toterg(box2n,en2n)
argl=-beta* ((enln-enlo) +
+ (npbox(1) +1) *1og(vln/vlo)/beta)
arg2=-beta* ((en2n-en2o) +
+ (npbox(2) +1) *1og(v2n/v2o)/beta)
if (ranf() .gt.exp(argl+arg2)) then
do i=l,npart
if (ibox(i).eq.) then
fact=boxlo/boxln
else
fact=box2o/box2n
endif
x(i)=x(i)*fact
enddo
endif
return
end
```

Comments on this algorithm: This algorithm ensures that, in each Monte Carlo step, detailed balance is obeyed. On average, we perform per cycle npart attempts to displace particles, nvol attempts to change the volume, and nswap attempts to swap particles between the two boxes. Subroutine incmove attempts to displace a randomly selected particle; this algorithm is very similar to Algorithm 2 (but remember that particles are in two different boxes). The subroutine incvol attempts to change the volume of the two boxes , the subroutine mc swap attempts to swap a particle between the two boxes, and subroutine sample samples the ensemble averages. The implementation of trial moves for particle displacement and volume change in Gibbs ensemble simulations is very similar to that of the corre- sponding trial moves in a normal N, V, T or N, P, T simulation. However, the attempts to exchange particles require some care. To ensure that detailed balance is obeyed, it is

important to first select at random from which box a particle will be removed and subsequently select a particle at random in this box. An alternative would be to first select one particle at random (from all N particles) and then try to move this particle to the other simulation box. However, in that case, the previously derived acceptance rule has to be replaced by a slightly different one [125]. The number of attempts to exchange a particle will depend on the conditions of the system. For example, it can be expected that close to the critical temperature, the percentage of accepted exchanges will be higher than close to the triple point. As a possible check whether the number of attempts is sufficient, calculate the chemical potential. Since the calculated energy of a particle that is to be inserted corresponds to just the test particle energy, the chemical potential can be calculated without additional costs.

Inspection of the partition function shows that one must allow for $n_1 = 0$ (box 1 empty) and $n_1 = N$ (box 2 empty) to calculate ensemble averages correctly. It is important therefore to ensure that the program can handle the case that one of the boxes is empty. The derived acceptance rule is constructed such that it indeed rejects trial moves that would attempt to remove particles from a box already empty.

The following figure shows the evolution of the density in the case of a LJ simulation
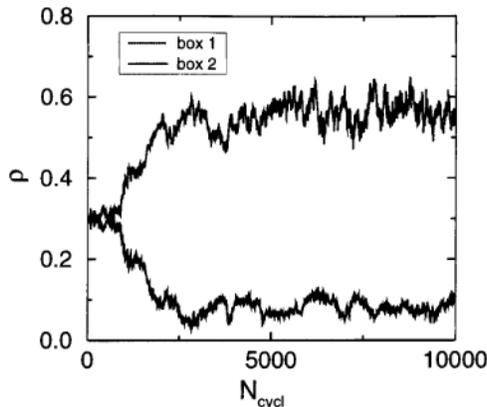
Figure 8.3: Density of the two boxes of the Gibbs ensemble as a function of the number of Monte Carlo cycles for a system of Lennard-Jones particles; the number of particles was $N = 256$ and temperature $T = 1.2$.

8 Tracing Coexistence Curves

Once a single point on the coexistence curve between two phases is known, the rest of that curve can be computed without further free energy calculations. A numerical technique for achieving this has been proposed by Kofke [149,150]. In its simplest form, Kofke's method is equivalent to the numerical integration of the Clausius-Clapeyron equation (although Kofke refers to his approach as Gibbs-Duhem integration). Let us briefly recall the derivation of the Clausius-Clapeyron equation. When two phases α and β coexist at a given temperature T and pressure P, their chemical potentials must be equal. If we change both the pressure and the temperature by infinitesimal amounts dP and dT, respectively, then the difference in chemical potential of the two phases becomes

$$d\mu_\alpha - d\mu_\beta = -(s_\alpha - s_\beta)dT + (\nu_\alpha - \nu_\beta)dP$$

Along the coexistence curve $\mu_\alpha = \mu_\beta$ and hence

$$\frac{dP}{dT}\Big|_{coex} = \frac{s_\alpha - s_\beta}{\nu_\alpha - \nu_\beta}$$

At coexistence $T\Delta s = \Delta h$, where h_α is the enthalpy per particle and hence

$$\frac{dP}{dT}\Big|_{coex} = \frac{\Delta h}{T\Delta \nu} \tag{12}$$

As Δh, $\Delta \nu$ and T all can be computed directly in a simulation, $\frac{dP}{dT}\big|_{coex}$ can be computed.

Note that if the slope of the coexistence curve is large, it becomes convenient to integrate the inverse equation

$$\frac{dT}{dP}\Big|_{coex} = \frac{T\Delta \nu}{\Delta h}$$

It is also possible to generalise the method adding one additional dimension that can couple with a modification of the Hamiltonian. In this case one can for example follow the evolution of the melting temperature at constant pressure upon a change in the potential. This is possible since when a coupling

parameter λ is introduced within the expression of the potential energy of the system, then the Gibbs free energy per particle becomes a function of λ, $g(T, V, \lambda)$ and the phase equilibrium

$$d\mu_\alpha - d\mu_\beta = 0 = -(s_\alpha - s_\beta)dT + (\nu_\alpha - \nu_\beta)dP + \left(\frac{\partial g}{\partial \lambda_\alpha} - \frac{\partial g}{\partial \lambda_\beta}\right)\delta\lambda$$

so that, if P is constant

$$-(s_\alpha - s_\beta)dT + \left(\frac{\partial g}{\partial \lambda_\alpha} - \frac{\partial g}{\partial \lambda_\beta}\right)\delta\lambda = 0$$

and

$$\frac{dT}{d\lambda}\Big|_{coex} = \frac{\left(\frac{\partial g}{\partial \lambda_\alpha} - \frac{\partial g}{\partial \lambda_\beta}\right)}{(s_\alpha - s_\beta)} = \frac{T\left(\frac{\partial g}{\partial \lambda_\alpha} - \frac{\partial g}{\partial \lambda_\beta}\right)}{(h_\alpha - h_\beta)}$$

We remember that

$$\frac{\partial g}{\partial \lambda} = -k_B T \frac{1}{Q_\lambda} \frac{\partial Q_\lambda}{\partial \lambda} = -k_B T < \frac{\partial H_\lambda}{\partial \lambda} >_\lambda$$

Kofke used a predictor-corrector algorithm to solve equation 12. If one of the two coexisting phases is the (dilute) vapour phase, it is convenient to cast equation 12 in a slightly different form:

$$\frac{d\ln P}{d1/T}\Big|_{coex} = \frac{\Delta h}{P\Delta\nu/T}$$

Kofke and co-workers have applied this method to locate the vapor-liquid [149,150] and solid-liquid coexistence curve of the Lennard-Jones fluid [240]. Other applications of the Kofke method can be found in [241-244]. It should be stressed that Gibbs-Duhem integration is in no way limited to the computation of coexistence curves in the P, T plane. A particularly important class of problems that can be treated in an analogous fashion is that where one studies the location of a phase transition as a function of the intermolecular interaction potential. For instance, Agrawal and Kofke have investigated the effect of a change of the steepness of the intermolecular potential in atomic

systems on the melting point (see Example 9). In the same spirit, Dijkstra and Frenkel [245, 246] studied the effect of a change in flexibility of rodlike polymers on the location of the isotropic nematic transition, Bolhuis and Kofke [247] the freezing of polydisperse hard spheres, and Bolhuis and Frenkel [248] the isotropic-solid coexistence curve of spherocylinders. Although Gibbs-Duhem integration is potentially a very efficient technique for tracing a coexistence curve, it is not very robust, as it lacks built-in diagnostics. By this we mean that the numerical errors in the integration of equation (9.2.2) may result in large deviations of the computed coexistence points from the true coexistence curve. Similarly, any error in the location of the initial coexistence points will lead to an incorrect estimate of the coexistence curve. For this reason, it is important to check the numerical stability of the scheme. This can be achieved by performing additional free energy calculations to fix two or more points where the two phases are in equilibrium. Meijer and E1 Azhar [249] have developed such a scheme in which the estimates of the coexistence densities are systematically improved by combining the Gibbs-Duhem scheme with a free energy difference calculation. In addition, the stability of the integration procedure can be checked by integrating backward and forward in the same interval. There is some evidence [244] that other integration schemes may be preferable to the predictor-corrector method used by Kofke. In fact, use of the predictor-corrector scheme to estimate phase-coexistence curves can lead to unphysical oscillations. These oscillations occur because of inevitable inaccuracies in our estimate of the initial coexistence point.

In some cases, for example, for systems containing long-chain molecules, percolating systems, or lattice models it is very difficult to perform volume changes. Escobedo and de Pablo [250] have shown that, under those conditions, it may be preferable to combine Gibbs-Duhem integration with the grand-canonical ensemble. In this scheme, μ and T are the independent variables, rather than P and T.

8.1 Runge-Kutta (Numerical Recipes)

The formula for the Euler method is

$$y_{n+1} = y_n + hf'(x_n, y_n) \tag{13}$$

which advances a solution from x_n to $x_{n+1} = x_n + h$. The formula is unsymmetrical: It advances the solution through an interval h, but uses derivative information only at the beginning of that interval. That means (and you can verify by expansion in power series) that the step's error is only one power of h smaller than the correction. There are several reasons that Euler's method is not recommended for practical use, among them, (i) the method is not very accurate when compared to other, fancier, methods run at the equivalent step size, and (ii) neither is it very stable.

Consider, however, the use of a step like Eq. 13 to take a "trial" step to the midpoint of the interval. Then use the value of both x and y at that midpoint to compute the "real" step across the whole interval. The following figure illustrates the idea.
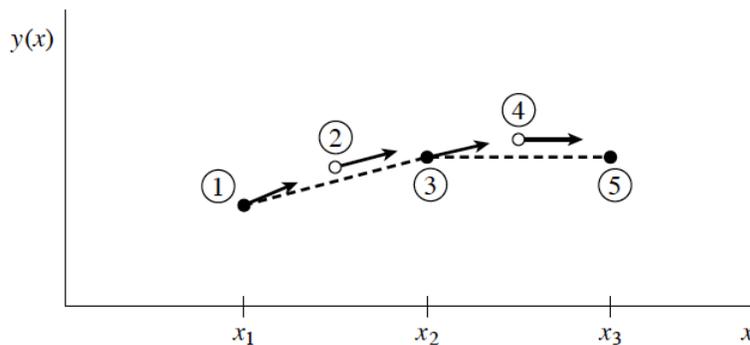

Figure 16.1.2. Midpoint method. Second-order accuracy is obtained by using the initial derivative at each step to find a point halfway across the interval, then using the midpoint derivative across the full width of the interval. In the figure, filled dots represent final function values, while open dots represent function values that are discarded once their derivatives have been calculated and used.

In equations,

$$k_1 = h f'(x_n, y_n)$$

$$k_2 = h f'(x_n + h/2, y_n + k_1/2)$$

$$y_{n+1} = y_n + k_2 + O(h^3)$$

As indicated in the error term, this symmetrization cancels out the first-order

error term, making the method second order. [A method is conventionally called nth order if its error term is $O(h^{n+1})$.] In fact, the previous equation is called the second-order Runge-Kutta or midpoint method.

We need not stop there. There are many ways to evaluate the right-hand side f(x, y) that all agree to first order, but that have different coefficients of higher-order error terms. Adding up the right combination of these, we can eliminate the error terms order by order. That is the basic idea of the Runge-Kutta method. Abramowitz and Stegun [1], and Gear [2], give various specific formulas that derive from this basic idea. By far the most often used is the classical fourth-order Runge-Kutta formula, which has a certain sleekness of organization about it:

$$
\begin{aligned}
k_1 &= hf'(x_n, y_n) \\
k_2 &= hf'(x_n + h/2, y_n + k_1/2) \\
k_3 &= hf'(x_n + h/2, y_n + k_2/2) \\
k_4 &= hf'(x_n + h, y_n + k_3) \\
y_{n+1} &= y_n + \frac{k_1}{6} + \frac{k_2}{3} + \frac{k_3}{3} + \frac{k_4}{6} + O(h^5)
\end{aligned}
\tag{14}
$$

The fourth-order Runge-Kutta method requires four evaluations of the right-hand side per step h (see Figure). This will be superior to the midpoint method if at least twice as large a step is possible with Eq. 14 for the same accuracy. Is that so? The answer is: often, perhaps even usually, but surely not always! This takes us back to a central theme, namely that high order does not always mean high accuracy. The statement "fourth-order Runge-Kutta is generally superior to second-order" is a true one, but you should recognize it as a statement about the contemporary practice of science rather than as a statement about strict mathematics. That is, it reflects the nature of the problems that contemporary scientists like to solve.

9 Direct coexistence method for liquid-crystal interfaces
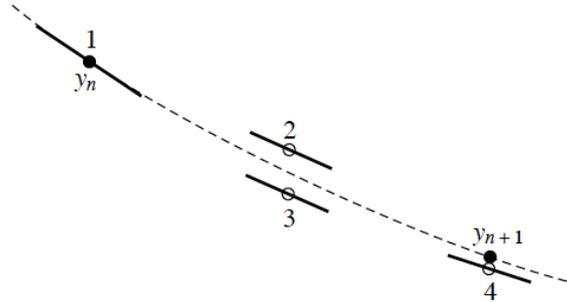
To be done

Figure 16.1.3.   Fourth-order Runge-Kutta method. In each step the derivative is evaluated four times: once at the initial point, twice at trial midpoints, and once at a trial endpoint. From these derivatives the final function value (shown as a filled dot) is calculated. (See text for details.)

10   Free energy of solids: the Einstein Crystal Method

A very good review of the methodology to calculate crystal free energies is provided in C Vega, E Sanz, J L F Abascal and E G Noya, J. Phys.: Condens. Matter 20 (2008) 153101.

The idea is to start from the analytically known free energy of Einstein Crystal, e.g. an harmonic oscillator of independent particles both in the particle position and in the particle orientation and then progressively convert it into the desired system. This is done by first turning on the system Hamiltonian and then releasing the Einsteins spring constants. For numerical reasons, the Einstein Crystal is defined at fixed center of mass and thus this constraint is lifted at the very end.

I sketch here the evaluation of the free energy for a molecule with symmetry C_{2v} as water, discussing at the end the changes that should be considered for different symmetries.

We define for each molecule two non-collinear versors: in the case of water,

Figure 1: Sequence of steps in the evaluation of the free energy

they could be the HH versor and the dipole versor, named respectively $\vec{a}$ and $\vec{b}$. We define a Einstein crystal in which molecules interact according to this Hamiltonian

$$H_{Eins} = H_{trans} + H_{rot}$$

with

$$H_{trans} = \lambda_{max}^t \sum_i (\mathbf{r}_i - \mathbf{r}_{i,0})^2$$

and

$$H_{rot} = \lambda_{max}^r \sum_i \left[\sin^2 \phi_{a,i} + \left(\frac{\phi_{b,i}}{\pi} \right)^2 \right]$$

Note that the rotational part of the Hamiltonian is invariant for the symmetry operation of the water molecule.

This system has a free energy that can be approximated analytically for $\beta\lambda_{max}^t \gg 1$ and $\beta\lambda_{max}^r \gg 1$. Consider the rotational part. The rotational free energy can be approximated for $\beta\lambda_{max}^r \gg 1$ as (in this limit two of the three Euler angles can be associated with ϕ_a and ϕ_b)

$$Q_{rot} = \frac{1}{8\pi^2} \int_0^\pi e^{-\beta\lambda_{max}\sin^2\phi_a} \sin\phi_a d\phi_a \int_{-\pi}^\pi e^{-\beta\lambda_{max}\left(\frac{\phi_b}{\pi}\right)^2} d\phi_b \int_0^{2\pi} d\gamma$$

and by defining $x = \cos\phi$ and $y = \frac{\phi_b}{\pi}$

$$Q_{rot} = \int_0^1 e^{-\beta\lambda_{max}(1-x^2)} dx \int_0^1 e^{-\beta\lambda_{max}y^2} dy$$

$$= \frac{\sqrt{\pi}e^{-\beta\lambda_{max}} Erfi(\sqrt{\beta\lambda_{max}})}{2\sqrt{\beta\lambda_{max}}} \frac{\sqrt{\pi}Erf(\sqrt{\beta\lambda_{max}})}{2\sqrt{\beta\lambda_{max}}}$$

$$\approx \frac{1}{2\beta\lambda_{max}} \frac{\sqrt{\pi}}{2\sqrt{\beta\lambda_{max}}}$$

So that

$$\beta F_{rot} = -\ln Q_{rot} = -\ln \frac{\sqrt{\pi}}{4} + \frac{3}{2} \ln \beta\lambda_{max}$$

Note that with the same approximation (large $\beta\lambda_{max}$) the average value of the potential energy associated with the rotational Hamiltionian (a value that can be checked in the simulation) is (numerator $\int He^{\beta H}$, denumerator $\int e^{\beta H}$)

$$< H_{rot} >= \frac{\frac{\lambda_{max}}{2(\beta\lambda_{max})^2}}{\frac{1}{2\beta\lambda_{max}}} + \frac{\frac{\frac{\sqrt{\pi}}{4}}{\beta^{3/2}}}{\frac{\frac{\sqrt{\pi}}{2}}{\sqrt{\beta\lambda_{max}}}} = k_BT + \frac{1}{2}k_BT$$

(or simply using $< H_{rot} >= -\partial\beta F_{rot}/\partial\beta$) Hence, if for the selected λ^r_{max}, the average potential energy associated with the rotational Hamiltonian is not 1.5 k_BT per molecule, then one needs to increase λ^r_{max}.

For the translational component, we will demonstrate later on that

$$Q^{CMfixed}_{transl} = P^{CM} \left(\frac{\pi}{\beta\lambda^t_{max}}\right)^{\frac{3(N-1)}{2}} N^{3/2}$$

P^{CM}, the integration over momenta, will cancel out when the constraint of the fixed COM is lifted. With no fixed COM,

$$Q_{trans} \equiv P \int e^{-\beta\lambda^t_{max} \sum_k (\mathbf{r}_k - \mathbf{r}_{0,k})^2} d\mathbf{r}^N = \left(\frac{\pi}{\beta\lambda^t_{max}}\right)^{\frac{3N}{2}}$$

$$\beta F_{trans} = -\ln Q_{trans}$$

10.1 The contribution of the interaction potential V_{pot}

For very large λ, the system behaves as an Einstein crystal, with an additional contribution arising from the underlying potential V_{pot}. If λ_{max} is very large and molecules are essentially localized, than this contribution is equivalent to the potential energy of V_{pot}. In this case $F_{pot,\lambda_{max}} \equiv< V_{pot} >_{\lambda_{max}}$

To be more precise, one can do two things:

- integrate (at fixed λ_{max}) over V_{pot} and calculate the average correction, e.g. perform a series of simulations with Hamiltonian

$$H = H_{Eins} + \gamma V_{pot}$$

for several values of γ between zero and one and calculate

$$F_{pot,\lambda_{max}} \equiv \int_0^1 < V_{pot} >_\gamma d\gamma$$

- evaluate in the simulation with H_{Eins} at λ_{max} the value of

$$F_{pot,\lambda_{max}} \equiv - \ln < \exp[-\beta V_{pot}] >_{\lambda_{max}}$$

Indeed, calling 1 the system with $H = H_{Eins}$ and 2 the system with $H = H_{Eins} + V_{pot}$, the difference in free energy

$$F_2 - F_1 = -k_B T \ln Q_2 + k_B T \ln Q_1 = -k_B T \ln \frac{Q_2}{Q_1} =$$

$$-k_B T \ln \frac{\int d\mathbf{r}^N \exp[-\beta(H_{Eins} + V_{pot})]}{\int d\mathbf{r}^N \exp[-\beta(H_{Eins})]}$$

$$= -k_B T \ln < \exp[-\beta V_{pot}] >_{\lambda_{max}}$$

We have thus as free energy of the COM constrained system interacting with the hamiltonian

$$H = H_{Eins} + V_{pot}$$

$$\beta F_{Einstein}^{CM} = \beta F_{rot} + \beta F_{trans}^{CM} + \beta F_{pot,\lambda_{max}}$$

10.2   Thermodynamic integration in the Eistein method

The free energy change along a thermodynamic path (in λ) is (assuming for simplicity $\lambda_{max}^t = \lambda_{max}^r = \lambda_{max}$. If this is not possible, then one can

defined the ratio $r \equiv \lambda^t_{max}/\lambda^r_{max}$ and and use $\lambda^r_{max} = \lambda_{max}$ and $\lambda^t_{max} = r\lambda_{max}$, including r in the definition of the Hamiltonian)

$$\beta F^{CM}_{\lambda_{max}} = \beta F_{\lambda=0} + \beta \int_0^{\lambda_{max}} < \frac{\partial H_\lambda}{\partial \lambda} >_\lambda d\lambda$$

where

$$H_\lambda = H^{CM}_{pot} + \lambda \sum_i (\mathbf{r}_i - \mathbf{r}_{i,0})^2 + \sum_i \lambda \left[\sin^2 \phi_{i,a} + \left(\frac{\phi_{i,b}}{\pi} \right)^2 \right]$$

so that (multiplying and dividing by λ)

$$\beta F^{CM}_{\lambda_{max}} = \beta F^{CM}_{pot} + \beta \int_0^{\lambda_{max}} \left\{ \lambda \sum_i (\mathbf{r}_i - \mathbf{r}_{i,0})^2 + \sum_i \lambda \left[\sin^2 \phi_{i,a} + \left(\frac{\phi_{i,b}}{\pi} \right)^2 \right] \right\} \frac{d\lambda}{\lambda}$$

so one has to integrate the rotational and translational average potential energy over $\ln \lambda$. Usually one fix a λ_{min} value below which the contribution to the integral is negligible.

When performing the simulations ad different values of λ one need to remember that the MC step has to be consistent with a change in energy of the order of $k_B T$. Hence, for large λ, the step must be of the order of $1/\sqrt{\lambda}$.

10.3 Releasing the COM

The difference in free energy between a system with frozen COM and free COM can be computed by calculating

$$\beta \Delta F^{CM \to NOCM} = -\ln \frac{Q^{CM}}{Q^{NOCM}} =$$

This last ratio is given by (imposing a δ function on the momenta and on the positions to enforce the COM conservation

$$\frac{\frac{1}{N!\hbar^{3N-1}} \int d\mathbf{p}^N e^{-\beta \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m_i}} \delta(\sum_{i=1}^{N} \mathbf{p}_i) \int d\mathbf{r}^N d\omega^N \exp[-\beta U(\mathbf{r}^N, \omega^N)]\delta(\sum_{i=1}^{N} m_i(\mathbf{r}_i - \mathbf{r}_{i,0}))}{\frac{1}{N!\hbar^{3N}} \int d\mathbf{p}^N e^{-\beta \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m_i}} \int d\mathbf{r}^N d\omega^N \exp[-\beta U(\mathbf{r}^N, \omega^N)]}$$

In the ratio all constants simplify (remains a $\hbar^3$ term only). The integration over the momenta gives a factor P^{CM}/P, where

$$P \equiv \int d\mathbf{p}^N \exp\left[-\beta \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m_i}\right]$$

The integration over the space of momenta of the unconstrained solid is simply the integral of a product of Gaussian functions, whose solution is (when all molecules have the same mass)

$$P = \left(\frac{2\pi m k_B T}{\hbar^2}\right)^{\frac{3N}{2}} = \left(\frac{1}{\Lambda}\right)^{3N}$$

The integration over positions can be performed considering that the energy of a system is not modified if the system is translated (while keeping the relative orientation of the molecules). The mathematical consequence of this is that $U(\mathbf{r}^N, \omega^N)$ can be rewritten as $U(\mathbf{r}'^N, \omega^N)$ where $\mathbf{r}'_i = \mathbf{r}_i - \mathbf{r}_1$. Let us locate the origin of the coordinate system in the center of mass, so that $N^{-1}\sum_{i=1}^{N} \mathbf{r}_{i,0} = \mathbf{R}_{CM}^0 = 0$ and let us perform a change of variables from $\mathbf{r}^N$ to $\mathbf{r}'_2....\mathbf{r}'_N, \mathbf{R}_{CM}$. We retains all coordinates from 2 to N and change the coordinate of molecule 1 in favor of the center of mass variable, through the relation $d\mathbf{r}_1 = N d\mathbf{R}_{CM}$ (e.g. the Jacobian of this transformation is N). With these changes one obtains

$$-\ln \frac{Q^{CM}}{Q^{NOCM}} = \frac{P^{CM}}{P} \frac{\int d\mathbf{r}^N d\omega^N \exp[-\beta U(\mathbf{r}^N, \omega^N)]\delta(\sum_{i=1}^{N} m_i(\mathbf{r}_i - \mathbf{r}_{i,0}))}{\frac{1}{\hbar^3} \int d\mathbf{r}^N d\omega^N \exp[-\beta U(\mathbf{r}^N, \omega^N)]} =$$

$$= \frac{P^{CM}}{P} \hbar^3 N \frac{\int d\mathbf{r}'_2....d\mathbf{r}'_N, d\mathbf{R}_{CM} d\omega^N \exp[-\beta U(\mathbf{r}'^N, \omega^N)]\delta(\mathbf{R}_{CM} - \mathbf{R}_{CM,0})}{N \int d\mathbf{r}'_2....d\mathbf{r}'_N, d\mathbf{R}_{CM} d\omega^N \exp[-\beta U(\mathbf{r}'^N, \omega^N)]}$$

The integration over $d\mathbf{r}'_2....d\mathbf{r}'_N d\omega^N$ is identical both in the numerator and in the denominator and, as a result,

$$= \frac{P^{CM}}{P}\hbar^3 \frac{\int \delta(\mathbf{R}_{CM})d\mathbf{R}_{CM}}{\int d\mathbf{R}_{CM}} = \frac{P^{CM}}{P}\hbar^3 \frac{1}{V_{explored}}$$

What is the volume $V_{explored}$ explored by the COM ? This is quite tricky. It comes out that it is the volume per particle. Indeed if the COM is allowed to explore larger volumes, then one generates one of the particle permutation originally included in the $N!$ contribution. Hence $V_{explored} = V/N$ and

$$-\ln \frac{Q^{CM}}{Q^{NOCM}} = -\ln \left[\frac{P^{CM}}{P}\hbar^3 \frac{N}{V}\right]$$

Thus, releasing the COM costs a free energy change equal to

$$\beta \Delta F^{CM->NOCM} = \ln \frac{P_{CM}\hbar^3}{P} - \ln \frac{V}{N}$$

where P and P_{CM} are the integration over moment space in the constrained and in the unconstrained model. Summing $\beta \Delta F^{CM->NOCM}$ to the free energy of the Einstein solid with frozen COM, the term $\ln P_{CM}$ disappears and one need only to calculate the unconstrained contribution from the momenta $\ln P$.

10.4 Partition function of the Einstein crystal with fixed center of mass

The translational contribution to the partition function of an Einstein crystal with fixed center of mass is

$$Q_{Eins,t}^{CM} = P^{CM} \int d\mathbf{r}^N \exp\left[-\beta \sum_{i=1}^N \lambda_{max}(\mathbf{r}_i - \mathbf{r}_{i,0})^2\right] \delta(\sum_{i=1}^N \mu_i(\mathbf{r}_i - \mathbf{r}_{i,0}))$$

where μ_i is the reduced mass $(m_i/\sum_j m_j)$ and where we have located the center of mass in the origin in the reference system, e.g. $\mathbf{r}_{CM} = 0$.

The term P_{CM} describes the integration over momenta with the constraint $\sum \mathbf{p}_i = 0$.

This integral can be expressed in a simpler way by defining a change of variable, $\mathbf{r}'_i = \mathbf{r}_i - \mathbf{r}_{i,0}$. The Jacobian of this change of variable is unity, and the configurational integral can be written as

$$Q_{Eins,t}^{CM} = P^{CM} \int d\mathbf{r'}^N \exp\left[-\beta \sum_{i=1}^{N} \lambda_{max}(\mathbf{r}'_i)^2\right] \delta(\sum_{i=1}^{N} m_i(\mathbf{r}'_i))$$

Transforming the Dirac δ as

$$\delta\left(\sum_{i=1}^{N} m_i(\mathbf{r}'_i)\right) = \frac{1}{(2\pi)^3} \int \exp\left[i\mathbf{k} \sum_{i=1}^{N} \mu_i \mathbf{r}'_i\right] d\mathbf{k}$$

the configurational integral can be written as

$$Q_{Eins,t}^{CM} = P^{CM} \frac{1}{(2\pi)^3} \int \exp\left[-\beta\lambda_{max} \sum_{i=1}^{N} \left((\mathbf{r}'_i)^2 - \frac{i\mathbf{k}}{\beta\lambda_{max}} \mu_i \mathbf{r}'_i\right)\right] d\mathbf{k} d\mathbf{r'}^N$$

By completing the squares (remembering $i * i = -1$)

$$(\mathbf{r}'_i)^2 - \frac{i\mathbf{k}}{\beta\lambda_{max}} \mu_i \mathbf{r}'_i = \left(\mathbf{r}'_i - \frac{i\mathbf{k}}{2\beta\lambda_{max}} \mu_i\right)^2 + \frac{k^2 \mu_i^2}{4\beta^2 \lambda_{max}^2}$$

and with another change of variable

$$\mathbf{r}''_i = \mathbf{r}'_i - \frac{i\mathbf{k}}{2\beta\lambda_{max}} \mu_i$$

the integral becomes

$$Q_{Eins,t}^{CM} = P^{CM} \frac{1}{(2\pi)^3} \int \exp\left[-\beta\lambda_{max} \sum_{i=1}^{N} \left((\mathbf{r}''_i)^2 + \frac{k^2 \mu_i^2}{4\beta^2 \lambda_{max}^2}\right)\right] d\mathbf{k} d\mathbf{r''}^N$$

The Jacobian of the transformation is one and so we have changed from $d\mathbf{k} d\mathbf{r'}^N$ to $d\mathbf{k} d\mathbf{r''}^N$. Indeed, for just one coordinate

$$r' = r'' + \frac{ik''m}{2\beta}$$

$$k' = k''$$

so that $\partial r'/\partial r'' = 1$, $\partial r'/\partial k'' = \frac{im}{2\beta}$, $\partial k'/\partial r'' = 0$ and $\partial k'/\partial k'' = 1$.

The integral can be split into two Gaussian integrals

$$Q_{Eins,t}^{CM} = P^{CM} \frac{1}{(2\pi)^3} \int \exp\left[-\beta\lambda_{max} \sum_{i=1}^{N} \mathbf{r''}_i^2\right] d\mathbf{r}''^N \int \exp\left[-\beta\lambda_{max} \frac{k^2 \sum_{i=1}^{N} \mu_i^2}{4\beta^2\lambda_{max}^2}\right] d\mathbf{k}$$

whose solution is

$$Q_{Eins,t}^{CM} = P^{CM} \frac{1}{(2\pi)^3} \left(\frac{\pi}{\beta\lambda_{max}}\right)^{3N/2} \left(\frac{4\pi\beta\lambda_{max}}{\sum_{i=1}^{N} \mu_i^2}\right)^{3/2}$$

Writing $(2\pi)^3 = (4\pi^2)^{3/2}$ and simplifying some quantities

$$Q_{Eins,t}^{CM} = P^{CM} \left(\frac{\beta\lambda_{max}}{\pi}\right)^{3/2} \left(\frac{\pi}{\beta\lambda_{max}}\right)^{3N/2} \left(\sum_{i=1}^{N} \mu_i^2\right)^{-3/2}$$

Summarizing, we have obtained that the partition function of an Einstein crystal with fixed center of mass is given by

$$Q_{Eins,t}^{CM} = P^{CM} \left(\frac{\pi}{\beta\lambda_{max}}\right)^{3(N-1)/2} \left(\sum_{i=1}^{N} \mu_i^2\right)^{-3/2}$$

When all molecules are identical $\sum_j \mu_j^2 = \sum_j \frac{m^2}{(Nm)^2}$ which is simply N^{-1}. Therefore, the previous equation can be simplified to

$$Q_{Eins,t}^{CM} = P^{CM} \left(\frac{\pi}{\beta\lambda_{max}}\right)^{3(N-1)/2} (N)^{-3/2}$$

which is the final expression for the free energy of an ideal Einstein crystal with fixed center of mass. An explicit expression for P_{CM} is not needed to get the free energy of the solid since it cancels out with a similar term.

10.5 ground state disorder

Sometime it is necessary also to add the degeneracy of the ground state. In the case of water this correspond to the so-called proton-disorder, an entropic contribution which was first estimated by Pauli as $\ln 3/2$

10.6 Final Result

The free energy of the model (including the ideal gas part) is thus given by four contributions, where the translational Einstein free energy has been summed up with the $\Delta F^{CM->NOCM}$ term to simplify the final result

$$
\begin{aligned}
\frac{\beta F^{pot}}{N} = &-\frac{1}{N} \ln \left[\left(\frac{1}{\Lambda} \right)^{3N} \left(\frac{\pi}{\beta \lambda_{max}} \right)^{\frac{3(N-1)}{2}} N^{\frac{3}{2}} \left(\frac{V}{N} \right) \right] \\
&+ \frac{\beta F_{rot}}{N} \\
&+ \beta < F_{pot} >_{\lambda_{max}} \\
&- \frac{\beta}{N} \int_0^{\lambda_{max}} < \frac{\partial H_\lambda}{\partial \lambda} >_\lambda d\lambda
\end{aligned}
\tag{15}
$$

10.7 Other symmetries

We have already given a convenient expression for the orientational field of a molecule with point group C_{2v} (for example water). Let us now give a convenient expression for other symmetries. For a molecule with a point group of type C_{nv} a convenient expression for H_{rot} is

$$
H_{rot}^{C_{nv}} = \lambda_{max}^r \sum_i \left[\sin^2 \left(\frac{n\phi_{a,i}}{2} \right) + \left(\frac{\phi_{b,i}}{\pi} \right)^2 \right]
$$

For a molecule with a point group of type D_{nh} a convenient expression is

$$H_{rot}^{D_{nh}} = \lambda_{max}^r \sum_i \left[\sin^2 \left(\frac{n\phi_{a,i}}{2} \right) + \sin^2 \left(\phi_{b,i} \right) \right]$$

For a molecule with point group O_h, a convenient expression is

$$H_{rot}^{O_h} = \lambda_{max}^r \sum_i \left[\sin^2 \left(\phi_{a,i,min} \right) + \sin^2 \left(\phi_{b,i,min} \right) \right]$$

where $\phi_{b,i,min}$ stands for the minimum angle between $\vec{b}_i^0$ and the six vectors connecting the reference point of the molecule with the six octahedral atoms/sites and an analogous definition for $\phi_{a,i,min}$

For a linear molecule only one vector (i.e. vector $\vec{b}_i^0$) is needed and the applied field should be of the form, for a $D_{\infty,h}$

$$H_{rot}^{D_{\infty,h}} = \lambda_{max}^r \sum_i \left[\sin^2 \left(\phi_{b,i} \right) \right]$$

For a $C_{\infty,\nu}$ molecule a convenient choice is

$$H_{rot}^{C_{\infty,\nu}} = \lambda_{max}^r \sum_i \left[\left(\frac{\phi_{b,i}}{\pi} \right)^2 \right]$$

The choice of an orientational field adapted to the symmetry of the molecule such as the ones proposed here is highly recommended. When this is done the energy with the external field is invariant to any of the symmetry operations of the molecule. Thus, a standard MC or MD program will provide correct values of the orientational contribution to the free energy. One interesting question is whether it is possible to use an external orientational field that does not reflect the symmetry of the molecule. The answer is, in principle, yes, but a special MC or MD code should be written for this purpose. Special moves should be added where the symmetry operations of the molecule are implemented. For instance, for water one should incorporate the C2 operation

that exchanges the positions of the two H atoms. Of course the energy of the molecule with the rest of the system is not affected by this operation.

10.8   General Implementation Issues

If all particles are coupled to the Einstein lattice, the crystal as a whole does not move. However, in the limit $\lambda \to 0$ there is no penalty for moving the particles away from their "Einstein" lattice position. As a consequence, the crystal as a whole may start to drift and the mean-squared particle displacement becomes on the order L^2. If this happens, the integrand in λ becomes sharply peaked around $\lambda = 0$. This would seem to imply that the numerical integration requires many simulations for low values of λ. This problem can be avoided if we perform the simulation under the constraint that the center of mass of the solid remains fixed. In this case, the mean square displacement tends to $< r^2 >_0$, the mean-squared displacement of a particle from its lattice site in the normal (i.e., interacting) crystal. To perform a Monte Carlo simulation under the constraint of a fixed center of mass we have to ensure that, if a particle is given a random displace- ment, all particles are subsequently shifted in the opposite direction such that the center of mass remains fixed. In practice, it is not very convenient to keep the center of mass in place by moving all particles every time a single- particle trial move is carried out. Rather, we update the center-of-mass position every time a single-particle trial move is accepted. We need to correct for the shift of the center of mass only when computing the potential energy of the harmonic springs connecting the particles to their lattice sites. In contrast, the calculation of the intermolecular potential can be carried out without knowledge of the position of the center of mass, as a shift of the center of mass does not change the distance between particles. It is convenient to distinguish between the coordinates $\mathbf{r}$) of a particle in the frozen center-of-mass reference system and the uncorrected coordinates $\mathbf{r}^u$. When computing the potential energy of the harmonic springs, we need to know $\sum_{i=1}^{N}(\mathbf{r}_i - \mathbf{r}_{0,i})^2$ To compute the distance of a particle i , to its lattice site, $(\mathbf{r}_i - \mathbf{r}_{0,i})$, we must keep track of the shift of the center of mass:

$$\Delta\mathbf{r}_i \equiv \mathbf{r}_i - \mathbf{r}_{0,i} = \mathbf{r}_i^u - \mathbf{r}_{0,i}^u - \Delta\mathbf{R}_{CM}$$

where $\Delta\mathbf{R}_{CM}$ denotes the accumulated shift of the center of mass of the system. Every time a particle is moved from $\mathbf{r}_i^u \rightarrow \mathbf{r}_i^u + \Delta\mathbf{r}$, $\Delta\mathbf{R}_{CM}$ changes to $\Delta\mathbf{R}_{CM} + \Delta\mathbf{r}/N$.

The computation of the change in energy of the harmonic interaction between all particles and their lattice site is quite trivial. Suppose that we attempt to move particle i , that is at a distance $\Delta\mathbf{r}_i$ from its lattice site $\mathbf{r}_{0,i}$) by an amount Δ_i. This causes a shift Δ_i/N in the center of mass. The change in the harmonic potential energy $\lambda\sum_k \Delta\mathbf{r}_i^2$ is

$$\Delta U_{Harm}(\lambda) = \lambda \sum_{i\neq j}[(\Delta\mathbf{r}_j - \Delta_i/N)^2 - \Delta\mathbf{r}_j^2] + \lambda[(\Delta\mathbf{r}_i + (1 - 1/N)\Delta_i)^2 - \Delta\mathbf{r}_i^2]$$

$$= \lambda\left(2\Delta\mathbf{r}_i \cdot \Delta_i + \frac{N-1}{N}\Delta_i^2\right) = \lambda\left(2\left[\mathbf{r}_i^u - \mathbf{r}_{0,i}^u - \Delta\mathbf{R}_{CM}\right] \cdot \Delta_i + \frac{N-1}{N}\Delta_i^2\right)$$

where, in the last line, we used the fact that $\sum_i \Delta\mathbf{r}_i = 0$. One more caveat should be considered: normally, when a particle moves out of the periodic box, the particle is put back at the other side of the box. However, when simulating a system with a fixed center of mass, moving a particle back into the original simulation box creates a discontinuous change in the position of the center of mass and hence a sudden change of the energy of the Einstein lattice. Therefore, in a simulation with a fixed center of mass, particles that move out of the original simulation box should not be put back in. In any event, the excursion that a harmonically bound particle can make is small and therefore there is no real need to put the particles back in the simulation box.

11   A recently proposed method to locate the coexistence point - The interface pinning method by U. Pedersen, J. Chem. Phys. 139 104102 (2013).

Let assume we have a system in which two phases coexist, close to coexistence. The system is prepared by splicing together two simulations each of

them created with its own phase. In the case of a liquid-crystal coexistence, one could first equilibrate the crystal and then melt the right half of the parallelepiped simulation box, to create a liquid coexisting with a solid.

Let us assume we are able to define an order parameter Q which has rather different values in the liquid Q_l and in the crystal Q_x phases. One possibility is offered by

$$S(\vec{q}_o) \equiv \frac{1}{N} | \sum_i \exp[i\vec{q} \cdot \vec{r}_i]|^2$$

where $\vec{q}_o$ is one of the reciprocal vector of the crystal. In the fluid $S(\vec{q}_o) \sim O(1)$, while in the crystal $S(\vec{q}_o) \sim O(N)$. Other order parameters, based on rotational invariant, are equally good.

To a first approximation, the order parameter in the system will be about (writing $N = N_l + N_x + N_i$)

$$Q \approx \frac{N_l Q_l + N_x Q_x + N_i Q_i}{N} = \frac{N_l(Q_l - Q_x) + NQ_x + N_i(Q_i - Q_x)}{N} \quad (16)$$

where Q_i is the order parameter of interfacial particles and N_i is their number

Now... let's suppose we run a simulation with a Hamiltonian that is

$$H = H_{potential} + \frac{1}{2}\kappa(Q - Q_0)^2$$

where $H_{potential}$ is the Hamiltonian of the system we are interested in and $\frac{1}{2}\kappa(Q - Q_0)^2$ is a biasing term that attempt to locate the order parameter of the system close to Q_0.

What is the distribution probability for Q resulting from this H ? Let's go by steps

The partition function is

$$Z = \int \exp[-\beta H]d\mathbf{R}^N = \int \exp[-\beta H_{potential}] \exp[-\beta \frac{1}{2}\kappa(Q(\mathbf{R}^N) - Q_0)^2]d\mathbf{R}^N$$

The probability of finding a fluctuation with order parameter Q can be calculated introducing the Dirac delta function

$$P(Q) \sim \int \exp[-\beta H_{potential}] \exp[-\beta \frac{1}{2}\kappa(Q(\mathbf{R}^N) - Q_0)^2] d\mathbf{R}^N \delta(Q - Q(\mathbf{R}^N))$$

$$= \exp[-\beta \frac{1}{2}\kappa(Q - Q_0)^2] \int \exp[-\beta H_{potential}] d\mathbf{R}^N \delta(Q - Q(\mathbf{R}^N))$$

where we can define

$$P_{potential}(Q) = \int \exp[-\beta H_{potential}] d\mathbf{R}^N \delta(Q - Q(\mathbf{R}^N))$$

as the probability of observing the order parameter Q in the absence of perturbation.

Formally we can associate to $P_{potential}(Q)$ a Q dependent free energy F via

$$P_{potential}(Q) = \exp[-\beta G_{potential}(Q)]$$

If Q_0 is not very far from the equilibrium Q, by expanding $G_{potential}(Q)$ around Q_0 at the second order

$$G_{potential}(Q) \approx G_{potential}(Q_0) + G'_{potential}(Q)(Q - Q_0) + \frac{1}{2}G_{potential}"(Q_0)(Q - Q_0)^2$$

one obtains

$$P(Q) \sim \exp[-\beta \frac{1}{2}\kappa(Q - Q_0)^2] \exp[-\beta(G_{potential}(Q_0) + G'_{potential}(Q)(Q - Q_0) + \frac{1}{2}G"_{potential}(Q_0$$

or, neglecting the constant which goes in the normalization

$$P(Q) \sim \exp[-\beta \frac{1}{2}\kappa(Q - Q_0)^2] \exp[-\beta G'_{potential}(Q_0)(Q - Q_0) + \frac{1}{2}G"_{potential}(Q_0)(Q - Q_0)^2)]$$

By making use of the relation $ax + bx^2 = b[(x + a/2b)^2 - a^2/4b^2]$, one can complete the square and predict that the fluctuations in Q are gaussians with an average

$$\bar{Q} = Q_0 - \frac{G'_{potential}(Q_0)}{\kappa + G"_{potential}(Q_0)}$$

The interesting thing is that if one pick $Q_0 \approx \frac{Q_l + Q_x}{2}$ and runs several simulations at different T or P and plot the resulting $P(Q)$, he/she will find that in some cases $\bar{Q}$ is larger that Q_0 and others is smaller than Q_0. The T or P value at which $\bar{Q} = Q_0$ indicates the coexistence point, e.g. the system is in thermodynamic equilibrium in the absence of the perturbation.

To prove this let's consider the behavior of $G_{potential}$. Defining G_l the free energy per particle of the liquid, G_x the free energy of the crystal and G_i the interface contribution to the free energy.

$$G = G_l N_l + G_x N_x + G_i = (G_l - G_x)N_l + G_x(N - N_i) + G_i \approx \Delta\mu N_l + constant$$

where we have assumed that there is only a week dependence of N_i e G_i on P and T. With a similar assumption one can invert Eq. 16 and find

$$\frac{NQ}{Q_l - Q_x} = N_l + constant$$

so that

$$G = \frac{NQ\Delta\mu}{Q_l - Q_x} + constant$$

In this approximation

$$G' = \frac{N\Delta\mu}{Q_l - Q_x} \qquad G" = 0$$

and

$$\bar{Q} = Q_0 - \frac{N\Delta\mu}{\kappa(Q_l - Q_x)}$$

That shows that at coexistence, where $\Delta\mu = 0$, $\bar{Q} = Q_0$. In principle, one can also estimate $\Delta\mu$ at the simulated T and P by inverting the previous equation. Close to coexistence (and far from critical points), where the approximations are ok,

$$\Delta\mu = \frac{(Q_0 - \bar{Q})\kappa(Q_l - Q_x)}{N}$$