

# Free-Energy Computation and First-Order Phase Transitions.

D. FRENKEL

*Physical Laboratory, Rijksuniversiteit Utrecht  
P.O. Box 80000, 3508 TA Utrecht, The Netherlands*

## 1. – Introduction.

The usual molecular-dynamics and Monte Carlo simulations yield statistical information about the « mechanical » properties of the system under consideration. The term mechanical property is reserved for explicit functions of the phase-space co-ordinates of a system. Examples are the potential energy of a given configuration,  $U(\mathbf{q}^N)$ , where  $\mathbf{q}^N$  stands for all (generalized) co-ordinates, or the virial  $V(\mathbf{q}^N) = \sum_{i=1}^N \mathbf{r}_i \cdot \mathbf{F}_i$ , where  $\mathbf{r}_i$  is the centre-of-mass co-ordinate of the  $i$ -th particle and  $\mathbf{F}_i$  the force on molecule  $i$  due to all other molecules. Knowledge of the ensemble or time average of such mechanical properties enables us to compute a number of important thermodynamic properties such as the internal energy  $E$  of a system, its pressure  $P$  and its heat capacity  $C_V$  (or  $C_P$ ). In contrast, it is not possible to obtain from a computer simulation direct information about « thermal » properties. Here the expression thermal properties is used to designate all properties whose value depends on the total volume of phase space that is accessible to the system under consideration. Typical examples are the entropy  $S$  of a system, its free energy  $F$  (here, and in what follows, I reserve the term free energy for the *Helmholtz* free energy; the Gibbs free energy, or free enthalpy, is denoted by  $G$ ) and the chemical potential  $\mu_\alpha$  of component  $\alpha$  in a mixture. The rest of this lecture will be concerned with computational techniques that enable us to compute thermal quantities. First, however, we have to answer two questions. The first question is: why can thermal properties not be obtained in the same way as mechanical properties? The second is: under what circumstances should one take the trouble of computing, say, the free energy of a system?

To answer the first question, let us consider a typical Monte Carlo (MC) simulation of a canonical ensemble. The present argument can be extended to other ensembles with minor modifications. In the canonical ensemble the

probability of finding a system of  $N$  particles, volume  $V$  and temperature  $T$  in a (hyper) volume  $d\mathbf{q}^N$  around a point  $\mathbf{q}^N$  in configuration space is given by

$$(1) \quad P(\mathbf{q}^N) d\mathbf{q}^N = \exp[-\beta U(\mathbf{q}^N)] d\mathbf{q}^N / Q_{NVT}.$$

Here  $\beta = 1/kT$  and  $Q_{NVT}$  is the configurational part of the partition function.  $Q_{NVT}$  is related to the free energy of the system by

$$(2) \quad F_{NVT} = -kT \ln(Q_{NVT}/N! \Lambda^{3N})$$

with  $\Lambda = (h^2/2\pi mkT)^{1/2}$ . In a Monte Carlo simulation with Metropolis (importance) sampling [1] the system performs a random walk through configuration space such that the probability of visiting a point  $\mathbf{q}^N$  is *proportional* to  $P(\mathbf{q}^N)$  but (unless one performs astronomically long runs) the constant of proportionality is unknown. To visualize this problem, it is helpful to think of the equivalent of the Monte Carlo method to measure the average depth  $\langle d \rangle$  of a river, a «mechanical» property, and its surface area  $A$ , a «thermal» property. Metropolis sampling in this case corresponds to taking a random step in the water and rejecting it if it takes you on to the riverbank but accepting it otherwise (see fig. 1). After every attempted step the depth  $d_i$  is recorded.

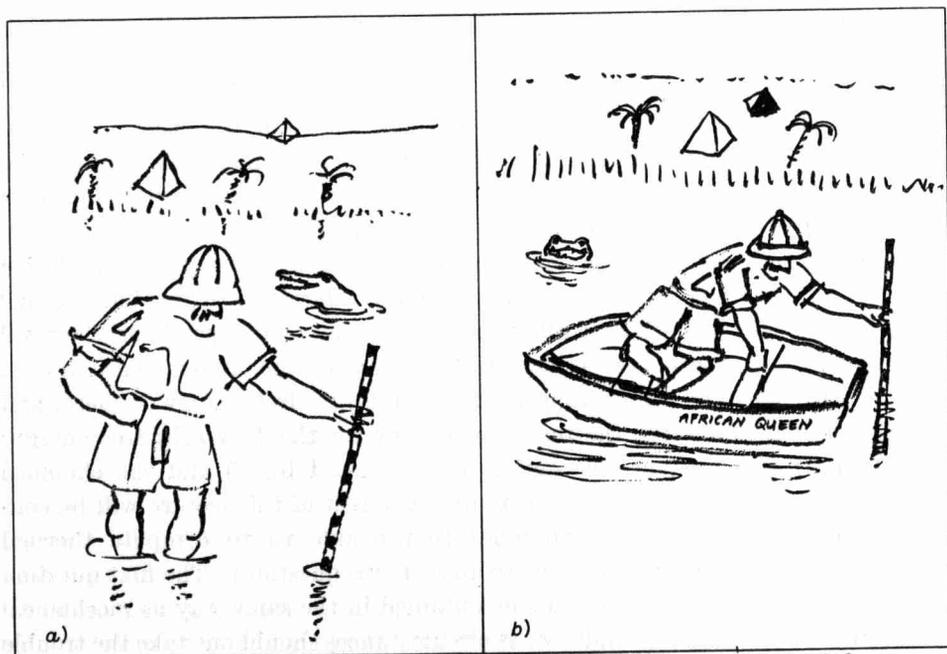


Fig. 1. — Measurement of the average depth of a river by the equivalents of importance sampling (a) and molecular-dynamics simulation (b). Note that neither method provides direct information about the area of the river. However, the frequency with which any known area of water is visited can be used to compute the total area [2].

The average depth of the river is obtained from

$$(3) \quad \langle d \rangle = \lim_{N \rightarrow \infty} \frac{1}{N} \sum_{i=1}^N d_i.$$

In practice the condition  $N \rightarrow \infty$  is replaced by the condition that  $N$  be sufficiently large that a representative (even if infinitesimal) fraction of all points in the river is visited. In contrast, no such procedure can be used to measure the surface area of the river, because  $A$  is not a «local» quantity like  $d$ . And the probability distribution does not help much either because, to take an extreme example, if only *one* point of area  $dA$  is sampled, one obtains a normalized probability 1 to be at that point; this result is indeed proportional to the correct probability  $dA/A$ , but that does not help much.

The only way to measure the area in this kind of Monte Carlo experiment is to determine the mean *recurrence* time, *i.e.* the number of steps that separate, on average, two visits to the same area  $dA$ . In statistical mechanical model systems this time, the Monte Carlo equivalent of the Poincaré time, is truly astronomical for all but the smallest systems. In fact, in a molecular-dynamics (MD) determination of the accessible volume of phase space the relevant time would indeed be the Poincaré time (see, however, subsect. 2'2 and ref. [2]). Having indicated that the computation of thermal properties must involve additional effort, it is useful to consider the second question formulated above: under what circumstances should one bother to compute thermal properties.

Apart from the obvious possibility that one may be interested in thermal properties for their own sake, *e.g.* to compare predictions of perturbation theories with computer experiments, there are situations where one has little choice but to compute thermal properties. The most important examples are phase equilibria and chemical equilibria. We recall that the condition for the co-existence of  $n$  phases at constant temperature and pressure is that the chemical potential  $\mu_\alpha$  of each molecular species has the same value in all phases, while the condition for chemical equilibrium at constant  $T$  and  $P$  is of the form  $\sum v_\alpha \mu_\alpha = 0$ , where the  $v_\alpha$  are the stoichiometric coefficients [3].

Of course, the fact that such equilibria put certain restrictions on the chemical potentials does not necessarily imply that one should explicitly calculate these quantities. After all, the great charm of computer simulation is that, given a sufficiently large system and a sufficiently long run, the system will find out for itself which phase and/or which chemical composition it prefers. The problem is that for most systems (though not all; see subsect 3'1) sufficiently large is too large and sufficiently long is too long for the average computing budget. More importantly, techniques exist which do the job at a lower price.

In the remainder of this lecture we will discuss a number of such techniques.

For general background information the reader is referred to [4-8] and, of course, to other lectures in the present volume.

## 2. – Methods to compute free energies.

2'1. *Preliminary remarks.* – In this section we discuss a number of computational techniques to compute absolute free energies and free-energy differences. Actually, there is no sharp distinction between the two because in the end almost all free-energy computations reduce to the evaluation of the free-energy *difference* between two states. Therefore, we reserve the term « absolute free-energy calculation » for cases where one of the two states under consideration is sufficiently simple that its absolute free energy can be evaluated analytically. In the examples to be discussed below we shall switch back and forth between free-energy computations and determinations of the chemical potential. For a one-compound system these computations are equivalent because all relevant thermal quantities are simply related ( $F = E - TS$ ,  $G = F + PV$ ,  $\mu = G/N$ ). However, for a multicomponent system it is really  $\mu_\alpha$ , the chemical potential of the  $\alpha$ -th species, that we are interested in.

2'2. *Direct methods.* – The free energy  $F$  of a system is related to its partition function  $Z$  by

$$(4) \quad F = -kT \ln Z,$$

which for a classical system reduces to

$$(2) \quad F = -kT \ln (Q/N! \Lambda^{3N}).$$

Hence in order to compute  $F$  we need to determine  $Q_{NVT}$ :

$$(5) \quad Q = \int d\mathbf{q}^N \exp[-\beta U(\mathbf{q}^N)],$$

where the notation is as in eq. (1).

The first point to note is that a direct numerical integration of eq. (5) is out of the question for all but the smallest systems. Consider, for instance, a « fluid » of  $N = 4$  hard spheres at a density of  $\frac{2}{3}\rho_0$ , where  $\rho_0$  is the density of regular close packing. If we use Simpson's method to evaluate the integral in eq. (5) with 10 points in all  $3(N-1)$  independent co-ordinates, then of the  $10^9$  evaluations of the integrand only  $\sim 5$  will yield a nonvanishing result. The situation gets much worse as one goes to larger systems.

Very close to the direct sampling method is the importance sampling technique devised by SALSBERG *et al.* [9] to determine the configurational integral of a 2D lattice gas. The method is based on the observation that  $V^N/Q$  can be written as

$$(6a) \quad V^N/Q = \int \exp[\beta U] \exp[-\beta U] d\mathbf{q}^N / \int \exp[-\beta U] d\mathbf{q}^N,$$

or

$$(6b) \quad V^N/Q = \langle \exp [\beta U] \rangle,$$

where the angular brackets stand for a canonical average. Note that  $Q$  has now been related to the average of a *mechanical* quantity and can, therefore, in principle, be obtained by importance sampling. The problem with this method, at least when applied to typical fluids and solids, is that large contributions to the average of  $\exp [\beta U]$  come from regions in configuration space where the sampling probability (*i.e.*  $\exp [-\beta U]$ ) is vanishingly small. Hence, unless all states including those with high energy are adequately sampled during a run, the method will give incorrect results. But such sampling involves at least as much work as sampling the whole of configuration space uniformly. Hence this method is of no practical use for classical fluids. For hard-core fluids the method even fails in principle. For further details see [6, 10-13].

A method that may be of some use for hard-core systems was devised by COLDWELL [14, 15]. This technique is based on the observation that the configurational integral of a system of  $N$  hard-core particles may be written as

$$(7) \quad Q_N = V \cdot \langle V_2 \rangle_1 \cdot \langle V_3 \rangle_{1,2} \cdot \dots \cdot \langle V_N \rangle_{1,2,\dots,N-1},$$

where  $\langle V_N \rangle_{1,\dots,N-1}$  stands for the average volume available to particle  $N$  in the presence of particles 1 through  $N-1$ . This approach is very similar in spirit to the early work of Byckling [16] (although apparently developed independently), but, because of the sophisticated bookkeeping of the volume available to the next particle to be added, it is more efficient. Coldwell's method was tried on 16 hard discs [14] and 25  $(2 + \frac{1}{2})$ -dimensional spherocylinders [15], and it appears to work satisfactorily up to rather high densities.

The main drawback of the method is that errors are introduced because all co-ordinates are discretized. In addition, the sheer complexity of the programming may discourage others from applying it to anything but the simplest systems.

A completely different method designed to evaluate the configurational integral of dense solids was developed by KRATKY [17]. In this approach the uniform sampling of configuration space used in a brute-force evaluation of  $Q$  is replaced by a nonuniform sampling. The weighting function is concentrated around the lattice positions of the individual particles and this restricts Kratky's method to systems with perfect translational order. The form of the weighting functions is optimized in an iterative fashion. Results were obtained in ref. [17] for hard-sphere crystals near close packing.

A final example of a direct method to compute a thermal average directly is the technique used by EDHOLM *et al.* [18] to evaluate the conformational entropy of a chain molecule. The approach is based on the expression for the

configurational entropy  $S_c$ :

$$(8) \quad S_c = -k \int P(\mathbf{q}^N) \ln P(\mathbf{q}^N) d\mathbf{q}^N,$$

where  $P(\mathbf{q}^N)$  is defined as in eq. (1).

In ref. [18] a discretized version of eq. (8) is used to obtain an estimate for conformational entropy of a chain molecule. The success of the method depends on the fact that at least a number of conformations are sampled sufficiently frequently to yield a reliable estimate of the probability of their occurrence. A very similar method was proposed earlier by MA [2].

**2'3. Particle insertion and related methods.** — We now turn to a number of more general and, on the whole, more powerful techniques to compute the chemical potential of a fluid. First among these is the so-called «particle insertion method», usually associated with the name of Widom, who formulated the general principles upon which this method is based [19], although actually a similar technique had first been employed by BYCKLING several years earlier [16]. The idea behind the particle insertion method is the following. Consider the expression for the chemical potential:

$$(9) \quad \mu = \left( \frac{\partial F}{\partial N} \right)_{v,T} = \lim_{\substack{N \rightarrow \infty \\ V \rightarrow \infty \\ N/V = \rho}} -kT \ln \left( \frac{Q_N}{Q_{N-1}} / \Lambda^3 N \right),$$

where we have used eq. (2). In the limit  $N/V \rightarrow 0$  the ratio  $Q_N/Q_{N-1} \rightarrow V$  and  $\mu$  reduces to the ideal-gas chemical potential:

$$(10) \quad \mu_{\text{id}} = kT \ln(\rho \Lambda^3),$$

where we have introduced the number density  $\rho = N/V$ . In (10) we have assumed the gas to be monatomic. Generalization to molecular systems is straightforward. Upon inserting (10) in (9) we obtain

$$(11) \quad \mu^{\text{ex}} \equiv \mu - \mu_{\text{id}} = -kT \ln(Q_N / V Q_{N-1}).$$

Hence the computation of the excess chemical potential  $\mu^{\text{ex}}$  is equivalent to the calculation of  $Q_N / Q_{N-1} V$ . The latter quantity can be cast in a form that can be evaluated by Monte Carlo sampling:

$$(12) \quad Q_N / Q_{N-1} V = \frac{1}{V} \frac{\int \exp[-\beta U(\mathbf{q}^{N-1})] \exp[-\beta V(\mathbf{q}_N; \mathbf{q}^{N-1})] d\mathbf{q}^N}{\int \exp[-\beta U(\mathbf{q}^{N-1})] d\mathbf{q}^{N-1}}.$$

In eq. (12)  $U(\mathbf{q}^{N-1})$  is the potential-energy function of the  $N-1$  particles,

while  $V(\mathbf{q}_N; \mathbf{q}^{N-1})$  represents the interaction of the  $N$ -th particle with all the others. Equation (12) can be written as the canonical average of a mechanical quantity:

$$(13) \quad Q_N/Q_{N-1} V = \frac{1}{V} \int d\mathbf{q}_N \langle \exp[-\beta V] \rangle_{N-1} .$$

Note that eq. (13) contains an average over  $\mathbf{q}^{N-1}$  co-ordinates which can be evaluated by importance sampling, and an integral over the  $N$ -th co-ordinate  $\mathbf{q}_N$  which must be sampled uniformly. In words:  $\exp[-\beta\mu_{ex}]$  is equal to the ensemble average of  $\exp[-\beta V_A]$ , where  $V_A$  is the interaction energy of the  $N-1$  particles with an extra particle added at a random position in the system.

In a hard-core fluid eq. (13) just gives the probability of acceptance of a Monte Carlo move consisting of the addition of an  $N$ -th particle at a random position in a system of  $N-1$  particles. Note that the particle insertion method is in no way limited to one-component systems. The particle insertion method as formulated by WIDOM has been used by several authors to study the thermal properties of atomic [20] and molecular [21, 22] fluids. An example is shown in fig. 2. An advantage of this technique is that it is very simple to insert in

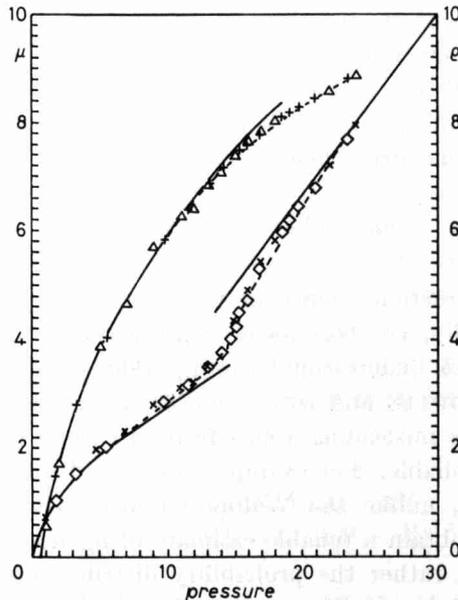


Fig. 2. - Chemical potential  $\mu$  of infinitely thin hard platelets of diameter  $\sigma$  [23] (pluses and triangles) determined by Widom's particle insertion method. The drawn curve through the data points was computed using the first five virial coefficients of hard platelets. The dashed curve was obtained by integration of the equation of state (squares and crosses) from low densities, using the Gibbs-Duhem relation. All quantities in reduced units,  $\sigma = 1, kT = 1$ .

existing Monte Carlo programs (including isobaric MC); with microcanonical simulations the situation is slightly more complicated (see appendix A). A problem with the Widom method is that the statistics become very poor as the density of the fluid under consideration is increased to the solidification point (for crystalline solids the method fails completely).

Several authors have developed techniques to extend the range of applicability of the particle insertion method. In a number of cases this was achieved by carrying out biased sampling, in the sense that the test particle is no longer inserted at random, but preferentially at « cavities » where it is most likely to be accepted [23-25]. As all these authors use either consciously or unconsciously « umbrella sampling », we will defer discussion to subsect. 2'6.

One rather different technique to compute  $\mu_{\text{ex}}$  in a dense 2D hard-disk fluid was developed by ZOLLWEG [26]. This author actually explicitly computes the fraction of the total area available for an additional disk in a fluid of  $N$  disks. This fraction is, of course, equal to the probability of acceptance of the insertion of the additional particle for a particular configuration.

This method works well even in the solid phase. However, the programming effort appears appreciable and no one has, as yet, found the courage (or the time) to extend Zollweg's method to continuous potentials or three-dimensional fluids.

Another extension of the particle insertion method is due to SHING and GUBBINS [27, 28]. Their approach is based upon the observation that  $\mu_{\text{ex}}$  could, in principle, also be obtained by considering the random *removal* of one particle from an  $N$ -particle system. In a way completely analogous the eqs. (11)-(13) above one may then derive that

$$(14) \quad \beta\mu_{\text{ex}} = \ln \langle \exp [+ \beta V_R] \rangle_N,$$

where  $V_R$  is the interaction energy of the particle to be removed with the  $N-1$  others. Actually, eq. (14) itself is not used by SHING and GUBBINS, as it leads to systematic underestimates of  $\mu_{\text{ex}}$ . This point has been investigated in some detail by POWLES and coworkers [29, 30]. The reason why eq. (14) taken at face value is misleading stems from the same cause that makes the Salsburg method unreliable. For example, for a hard-core fluid eq. (14) would always yield  $\mu_{\text{ex}} = 0$ , unlike the Widom method. The method that SHING and GUBBINS use to obtain a reliable estimate of  $\mu_{\text{ex}}$  does not use  $\langle \exp [\beta V_R] \rangle$  or  $\langle \exp [-\beta V_A] \rangle$  but rather the probability distributions of  $V_R$  and  $V_A$ . As this method turns out to be identical to Bennett's overlapping-distribution method [31], we postpone the discussion to subsect. 2'5.

A method closely related to the particle insertion method is the cavity distribution method described in the same paper of Widom [19]. It was first formulated by HOOVER and POIRIER [32] and later extended by MEERON and SIEGERT [33].

The gist of the method is that one may show that the cavity function  $y(r)$  is related to the correlation function of  $\exp[-\beta V_A]$ :

$$(15) \quad y(r) \equiv \exp[\beta\varphi(r)]g(r) = \exp[2\beta\mu_{\text{ex}}] \langle \exp[-\beta V_A(0)] \exp[-\beta V_A(r)] \rangle,$$

where  $\varphi(r)$  is the intermolecular potential,  $g(r)$  the radial distribution function and  $V_A(\mathbf{r})$ , as before, the interaction of a test particle at  $\mathbf{r}$  with the molecules already present. For hard-core particles, in the limit  $r \rightarrow 0$ , eq. (15) reduces to

$$(16) \quad y(0) = \exp[\beta\mu_{\text{ex}}].$$

This indicates that  $\mu_{\text{ex}}$  can be determined by measuring the cavity distribution function down to  $r = 0$ . An example of such a computation can be found in ref. [34]. The cavity method runs into the same problems at high densities as the particle insertion method. Moreover, it is less simple to program. It seems unlikely that the cavity method will prove a powerful computational tool to measure free energies of simple fluids.

2.4. *Grand canonical ensemble.* – Rather similar in implementation, though different in spirit than the particle insertion and extraction methods of the previous subsection is the grand canonical (GC) ensemble method. This method, first introduced by NORMAN and FILINOV [35], was later extended and improved by a number of workers [20, 36-43]. Here we shall sketch the approach suggested by ADAMS [20, 36-38], but modified for didactical reasons.

In the grand canonical ensemble  $T$ ,  $V$  and  $\mu$  are held fixed, while  $E$ ,  $P$  and  $N$  may fluctuate. The basic idea behind grand canonical Monte Carlo (GCMC) is that  $\mu$  is known *a priori*, because it is imposed, and the simulation then yields values for  $\langle N \rangle$  etc. It is convenient to consider the GC ensemble as a system of volume  $V$  which can exchange heat and particles with a very large reservoir which contains an ideal gas of the same particles. The volume of the reservoir is  $V' \gg V$ . The total number of particles is  $M$ . The partition function for this joint system is given by

$$(17) \quad \frac{Q_M(V, V'; T)}{M!} = \sum_{N=0}^M \frac{Q_N(V)}{N!} \frac{Q_{M-N}(V')}{(M-N)!},$$

where it is understood that  $M \rightarrow \infty$ ,  $V' \rightarrow \infty$ ,  $M/V' \rightarrow \Lambda^{-3} \exp[\beta\mu]$  (remember, in  $V'$  we have an ideal gas). Now we could follow the usual procedure, *i.e.* to divide (17) by  $Q_M(V')/M!$  and obtain the GC partition function for the small system  $V$ , but this is not what we shall do. We just ask ourselves: what is the probability of finding  $N$  particles in a volume of  $d\mathbf{q}^N$  around  $\mathbf{q}^N$  in  $V$  and  $M-N$  particles in a volume  $d\mathbf{q}^{M-N}$  around  $\mathbf{q}^{M-N}$  in  $V'$ ? Clearly, this probability

is given by

$$(18a) \quad P(\mathbf{q}^M) d\mathbf{q}^M = Q_M^{-1}(V, V'; T) \exp[-\beta U(\mathbf{q}^N)] d\mathbf{q}^N d\mathbf{q}^{M-N} \frac{M!}{N!(M-N)!}.$$

Now it is convenient to switch to reduced co-ordinates  $\boldsymbol{\tau}$ , such that both in  $V$  and in  $V'$  all components of  $\boldsymbol{\tau}$  range from 0 to 1:  $\boldsymbol{\tau}^N = \mathbf{q}^N/V^N$  and  $\boldsymbol{\tau}^{M-N} = \mathbf{q}^{M-N}/V'^{(M-N)}$ . This constitutes a one-to-one mapping of reduced co-ordinates in  $V$  and  $V'$ . In terms of  $\boldsymbol{\tau}^M$ ,

$$(18b) \quad P(\boldsymbol{\tau}^M) V^N V'^{(M-N)} d\boldsymbol{\tau}^M = Q_M^{-1}(V, V'; T) \frac{V^N V'^{(M-N)} M!}{N!(M-N)!} \exp[-\beta U(\boldsymbol{\tau}^N)] d\boldsymbol{\tau}^M.$$

Now we can ask for the ratio  $R$  of probability (18b) to the probability where one particle has been moved from  $V'$  to the same reduced position in  $V$ .

It is easy to see that this ratio must be

$$(19) \quad R_{N+1,N} = \frac{V}{N+1} \frac{M-N}{V'} \exp[-\beta(U(\boldsymbol{\tau}^{N+1}) - U(\boldsymbol{\tau}^N))]$$

or, keeping in mind that  $M \gg N$  and  $M/V' = A^{-3} \exp[\beta\mu]$ ,

$$(20) \quad R_{N+1,N} = \frac{V}{N+1} A^{-3} \exp[\beta(\mu - \Delta U)],$$

where we have written  $\Delta U$  for  $U(\boldsymbol{\tau}^{N+1}) - U(\boldsymbol{\tau}^N)$ . Similarly, the corresponding ratio of probabilities where one particle is moved from  $V$  to  $V'$  is given by

$$(21) \quad R_{N-1,N} = \frac{N}{V} A^3 \exp[-\beta(\mu - U(\boldsymbol{\tau}^N) + U(\boldsymbol{\tau}^{N-1}))].$$

Hence, we can sample a GC as long as the relative probability with which particles are added or removed obeys eqs. (20) and (21). One method to achieve this is to use the conventional Metropolis sampling for the probability of acceptance of particle insertions and removals:

$$(22) \quad \begin{cases} P_{\text{acc}}(N+1, N) = \min[1, R_{N+1,N}], \\ P_{\text{acc}}(N-1, N) = \min[1, R_{N-1,N}]. \end{cases}$$

In eq. (22) it is assumed that the numbers of *attempts* to add or remove a particle are equal. In addition to particle-number-changing moves one performs normal MC sampling at constant  $N$ . One final remark on eqs. (20), (21). Note that, if we denote the, *a priori* unknown, average density in  $V$  by  $\rho = \langle N \rangle / V$ , then  $\beta\mu_{\text{id}}(\rho) = \ln(\langle N \rangle A^3 / V)$ . Inserting this in (20), (21) results in the slightly

simpler expressions

$$(23) \quad \begin{cases} R_{N+1,N} = \exp[\beta(\mu_{\text{ex}} + \beta^{-1} \ln \langle N \rangle - \Delta U)] / (N + 1), \\ R_{N-1,N} = \exp[-\beta(\mu_{\text{ex}} + \beta^{-1} \ln \langle N \rangle + \Delta' U)] N. \end{cases}$$

In a simulation the quantity  $B = \beta\mu_{\text{ex}} + \ln \langle N \rangle$  is the control variable.

At the end of the run  $\mu_{\text{ex}}$  is computed using the value of  $\langle N \rangle$  obtained during the simulation. The GCMC method has the attractive feature that it is possible to carry out simulation at a particularly interesting value of  $\mu$ , *e.g.* at a phase transition. GCMC is easy to extend to multicomponent systems, and has been generalized to ionic systems [42, 43] where particles can only be inserted or removed in neutral groups.

There are several problems with the GCMC method that should be mentioned.

The first is easily eliminated if one is aware of it. It was noted [36] that the results of the GCMC are very sensitive to the quality of the random-number generator used. The second is actually the same problem that limited the applicability of particle insertion methods at high densities (see subsect. 2'3). At typical liquid densities the acceptance of particle-number-changing moves becomes very low. As a consequence it may be impossible to reach the correct equilibrium density in a reasonable time. MEZEI [41] has succeeded in improving the efficiency of the GCMC at high densities by preferentially inserting particles in « cavities ». It is, however, not obvious that this method really results in a dramatic saving of computing time.

The final point to note is that the results for  $\mu_{\text{ex}}$  obtained by the GCMC show a pronounced system size dependence [20]. This may well be due to the fact that, for most systems, the thermal properties exhibit a  $\ln N/N$  dependence. Usually one can eliminate this problem by computing excess properties (*e.g.*  $\mu_{\text{ex}}$ ) with respect to a reference system *with the same number of particles*.

However, in the conventional GCMC method the reference system is the *infinite* ideal gas. (The same holds, by the way, for the Widom method.) Hints that this is indeed at the root of the problem came from the work of Yao *et al.* [40] who carried out the GCMC on a system with an upper limit on the total number of particles that could be inserted. These authors found no evidence for system size dependence of  $\mu$ .

To my knowledge no one has tried to perform a truly finite-size GCMC, starting from eq. (18b), with  $M$  chosen such that  $\langle N \rangle \approx M - \langle N \rangle$ .

**2'5. Overlapping distributions and related methods.** – Suppose we have, in one way or another, obtained the free energy  $F_0$  of a system with potential-energy function  $U_0$  at temperature  $T = (k\beta)^{-1}$  and volume  $V$ .

We wish to know the free energy of a closely related system with potential-energy function  $U_1 = U_0 + \Delta U$ , or of the same system but at a different temperature  $T'$ . Let us, for simplicity, concentrate on the first case. The

free-energy difference between systems 1 and 0 is given by

$$(24) \quad F_1 - F_0 = -kT \ln(Q_1/Q_0).$$

But  $Q_1/Q_0$  can be written as an expectation value of  $\exp[-\beta\Delta U]$ :

$$(25) \quad Q_1/Q_0 = \frac{\int \exp[-\beta(U_0 + \Delta U)] d\mathbf{q}^N}{\int \exp[-\beta U_0] d\mathbf{q}^N} = \langle \exp[-\beta\Delta U] \rangle_0$$

and hence

$$(26) \quad F_1 - F_0 = -kT \ln \langle \exp[-\beta\Delta U] \rangle_0.$$

It is convenient to discuss eq. (26) in terms of the potential-energy density function  $\gamma_0(U)$ , first introduced by McDONALD and SINGER [44-46].

$\gamma_0(U)$  is defined as

$$(27) \quad \gamma_0(X) = V^{-N} \int \delta(X - U_0(\mathbf{q}^N)) d\mathbf{q}^N.$$

The probability of finding the system 0 at inverse temperature  $\beta$  in a range  $dU$  around  $U$  is given by

$$(28) \quad f_0^r(U) dU = \frac{\gamma_0(U) V^N \exp[-\beta U] dU}{Q_0(T)}.$$

Now whereas  $\gamma_0(U)$  is a very rapidly increasing function of  $U$ ,  $f_0^r(U)$  is sharply peaked around a value  $U'$ , such that  $(\partial \ln \gamma_0 / \partial U)_{U'} = \beta$ . Now suppose we wish to use eq. (25) to determine the free-energy difference between two state points of the same system at temperatures  $T$  and  $T'$ .

Then, from eqs. (25) and (28) we have

$$(29) \quad Q(T')/Q(T) = \frac{\int \gamma_0(U) \exp[-\beta' U] dU}{\int \gamma_0(U) \exp[-\beta U] dU}.$$

From eq. (29) it follows that, if one knows the (unnormalized)  $\gamma_0(U)$  over a wide range of  $U$ 's, one can compute free-energy differences over a wide range of temperatures. This is precisely what McDONALD and SINGER did. Unfortunately, computing  $\gamma_0(U)$  is not easy, and the way it was obtained in ref. [45] resembles later multistage and umbrella sampling methods (see below). It is much easier to obtain  $f_0(U)$ . In terms of  $f_0^r(U)$ , the ratio  $Q(T')/Q(T)$  is given by

$$(30) \quad Q(T')/Q(T) = \int f_0(U) \exp[-\beta\Delta U] dU.$$

Equation (30) follows directly from eq. (28), with  $\Delta U = U(\beta'/\beta - 1)$ . Note that the (normalized) distribution  $f_0(U)$  can be obtained directly in a normal

(Metropolis) MC run. The applicability of eq. (30) is limited by the fact that, as the difference between  $\beta'$  and  $\beta$  increases, the maximum of  $f_0(U) \exp[-\beta \Delta U]$  shifts to values of  $U$  where  $f_0(U)$  itself is very small and hence inadequately sampled during a normal Monte Carlo run. When this occurs eq. (30) and hence eqs. (25), (26) cease to be useful. Examples of the direct application of eq. (26) can be found in ref. [47, 48]. Several methods have been devised to extend the applicability of eqs. (25), (26). The most straightforward of these is the so-called multistage sampling technique [6, 11, 49, 50]. This method is basically aimed at obtaining information about  $\gamma_0(U)$  over a wide range of  $U$ 's by sampling  $f_0^x(U)$  over a range of temperatures. The idea is that, as  $\gamma_0(U) \sim \exp[\beta U] f_0^x(U)$ ,  $\gamma_0(U)$  can be obtained over a range of energies by computing  $f_0^x(U)$  for several different temperatures. These temperatures should be chosen sufficiently differently that they all probe a different range of  $U$ 's, yet sufficiently close that there is a substantial range of  $U$ 's where the successive  $f_0^x(U)$  overlap. This latter requirement guarantees that the unnormalized function  $\exp[\beta U] f_0^x(U)$  can be joined smoothly to  $\exp[\beta' U] f_0^{x'}(U)$ ; in this way one obtains an unnormalized function  $C\gamma_0(U)$  from which free-energy differences can be computed using eq. (29).

BENNETT [31] has presented a more general framework in which to discuss the relation between free-energy differences and potential-energy distributions. Consider two  $N$ -particle systems 0 and 1 with potential-energy function  $U_0(\mathbf{q}^N)$  and  $U_1(\mathbf{q}^N)$ . During a simulation on system 0 one may accumulate a histogram of  $p_0(\Delta U)$  which measures the probability density of observing a potential-energy difference  $\Delta U = U_1 - U_0$ . Conversely, during a simulation on system 1 one may obtain the corresponding probability density  $p_1(\Delta U)$ . Both  $p_0$  and  $p_1$  are normalized to 1, which equals the probability to observe *any* potential-energy difference.  $p_0$  and  $p_1$  can be written as normal canonical averages:

$$(31) \quad p_1(\Delta U) = Q_1^{-1} \int \exp[-\beta(U_0 + \Delta U)] \delta(U_1 - U_0 - \Delta U) d\mathbf{q}^N = \\ = (Q_0/Q_1) \exp[-\beta \Delta U] p_0(\Delta U),$$

or

$$(32) \quad p_1(\Delta U)/p_0(\Delta U) = \exp[\beta(\Delta F - \Delta U)],$$

where  $\Delta F = F_1 - F_0$  is the free-energy difference between 1 and 0. What eq. (30) says is that, wherever  $p_0$  and  $p_1$  overlap, the ratio of the two can be used to compute the free-energy difference  $\Delta F$ . For hard-core systems one need only keep track of the values of  $p_0$  and  $p_1$  at  $\Delta U = 0$ . The ratio  $p_1(0)/p_0(0)$  then measures the fraction of the configuration space of 1 that is accessible to 0, divided by the fraction of configuration space of 0 that is accessible to 1. In this case eq. (32) can be given a simple geometric interpretation (see fig. 3). It should be added that, although eq. (33) expresses a relation between the free

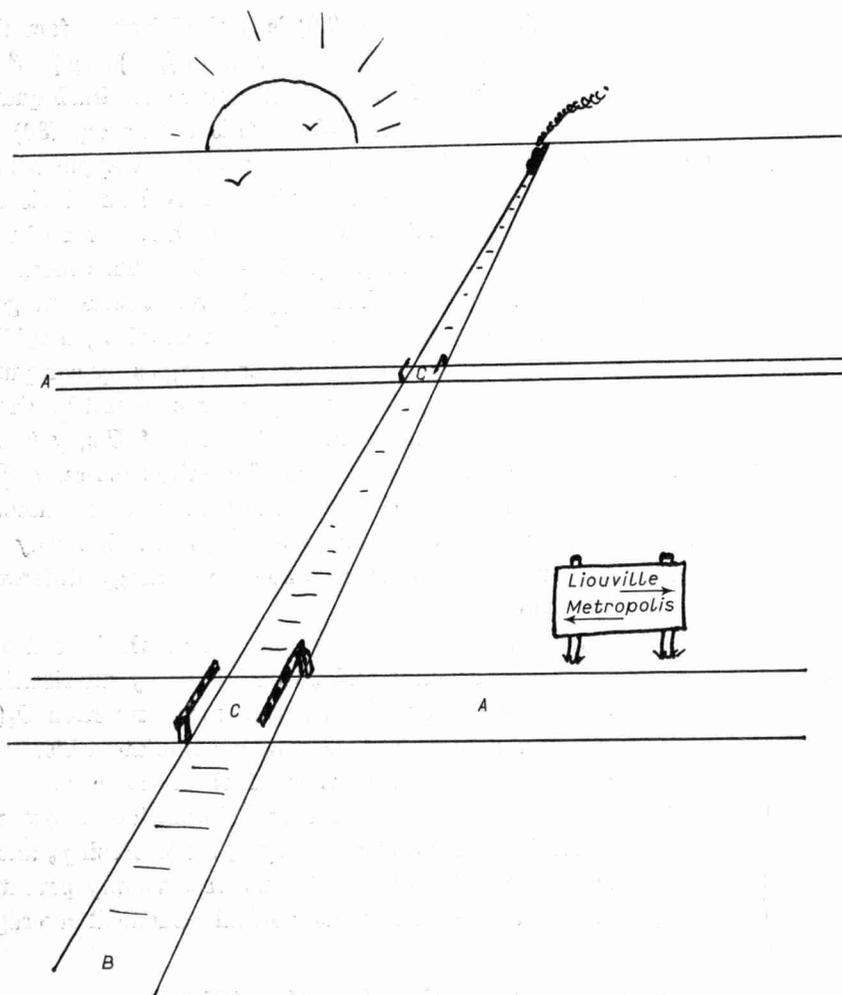


Fig. 3. — Consider two subvolumes of phase space, volume *A* (« roads ») and volume *B* (« railroads »). The intersection of *A* and *B* is *C* (« level crossings »). If the level crossings account for 1% of the area of all railroads and for 0.1 % for the total road area, then the area of all roads is ten times the area of all railroads.

energy of two  $N$ -particle systems, one or more of the particles in either system may be « fictitious » in the sense that they do not interact with any of the other particles. In particular, one may use eqs. (30)-(32) to derive the Shing-Gubbins expression for the chemical potential (see subsect. 2'3).

To this end consider an  $N$ -particle system 1, and system 0 consisting of  $N-1$  interacting particles and one fictitious particle. In that case it is easy to show that

$$(33) \quad p_1(\Delta U)/p_0(\Delta U) = \exp[\beta(\mu_{ex} - \Delta U)].$$

This is the expression used in ref. [27-29] to compute  $\mu_{\text{ex}}$ . BENNETT [31] argues that in order to obtain  $\Delta F$  it is often not even necessary to have  $p_1$  and  $p_0$  overlap at all, as long as both are reasonably smooth functions of  $\Delta U$  and the gap between them is not too wide. The procedure suggested by BENNETT is to plot

$$f_1(\Delta U) \equiv \ln p_1(\Delta U) + \frac{1}{2}\beta \Delta U \quad \text{and} \quad f_0(\Delta U) \equiv \ln p_0(\Delta U) - \frac{1}{2}\beta \Delta U$$

vs.  $\Delta U$ . From eq. (32) it follows that

$$(34) \quad f_1(\Delta U) = f_0(\Delta U) + \beta \Delta F.$$

Hence one can obtain  $\Delta F$  by fitting  $f_0$  to a polynomial  $P(\Delta U)$  and fitting  $f_1$  to the same polynomial plus a constant offset  $X$ ; the value of  $X$  that yields the best fit is the best estimate for  $\beta \Delta F$ . If the gap between  $p_0$  and  $p_1$  is so wide that straightforward interpolation is not sufficiently accurate, eq. (32) may be combined with multistage sampling in which one carries out a number of simulations on systems with potential-energy function intermediate between  $U_0$  and  $U_1$ , e.g.  $U(\lambda) = \lambda U_1 + (1 - \lambda) U_0$ . By choosing a sufficient number of intermediate  $\lambda$ -values one can always guarantee that the successive distributions will indeed overlap (see fig. 4). Examples of applications of the overlapping-distribution method can be found in ref. [51-53], while the extension to quantum systems is discussed in ref. [54]. A second method to compute free-energy differences is also due to BENNETT [31]. This method is usually referred to as the acceptance ratio method. The starting point here is the identity

$$(35) \quad Q_0/Q_1 = (Q_0/Q_1) \frac{\int W(\mathbf{q}^N) \exp[-\beta(U_0 + U_1)] d\mathbf{q}^N}{\int W(\mathbf{q}^N) \exp[-\beta(U_0 + U_1)] d\mathbf{q}^N},$$

where  $W(\mathbf{q}^N)$  is an, as yet unspecified, weight function. Equation (35) can be rewritten as

$$(36) \quad \exp[\beta(F_1 - F_0)] = \langle W \exp[-\beta U_0] \rangle_1 / \langle W \exp[-\beta U_1] \rangle_0.$$

BENNETT then proceeds to show that the choice of  $W$  that leads to the best estimate of  $\Delta F = F_1 - F_0$  is of the form

$$(37) \quad W(\mathbf{q}^N) = C(Q_0/n_0 \exp[-\beta U_1] + Q_1/n_1 \exp[-\beta U_0])^{-1}.$$

In eq. (37)  $n_0$  ( $n_1$ ) stands for the number of statistically independent samples in system 0 (1) on which the expectation values of  $\langle W \exp[-\beta U_1] \rangle_0$  and  $\langle W \exp[-\beta U_0] \rangle_1$  are based. Of course,  $Q_0$  and  $Q_1$  are not known *a priori* and it might seem, therefore, that eq. (37) is of little use. However, inserting eq. (37)

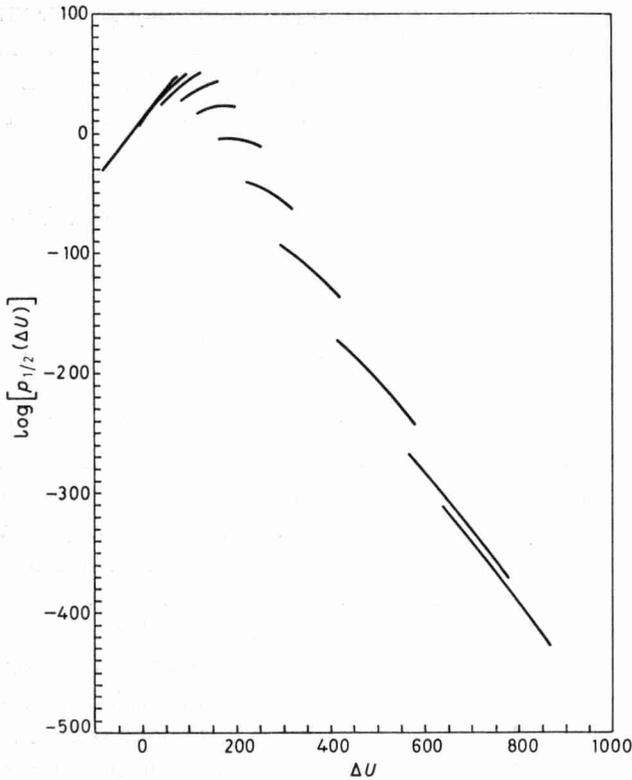


Fig. 4. — Multistage overlapping-distribution method to determine the free-energy difference between f.c.c. « helium » crystal (see ref. [55]) and a corresponding Einstein crystal. The plot shows  $\ln(p_{\lambda}(\Delta U)) + \beta \Delta U$ , where  $\Delta U$  is the potential-energy difference between a system with potential energy  $U(\lambda)$  and a system with  $\lambda = \frac{1}{2}$ . The sum of the discontinuities between successive curves yields  $(F_{f.c.c.} - F_{Einstein})/NkT = 0.8640$ , which is within the estimated error of the thermodynamic-integration value  $\Delta F = 0.8638$  (see subsect. 3'3).

in (36) we obtain

$$(38) \quad \exp[\beta \Delta F] = \frac{\langle f(\beta(U_0 - U_1) + C) \rangle_1}{\langle f(\beta(U_1 - U_0) - C) \rangle_0} \exp[C],$$

where  $f(X)$  is the Fermi function  $1/(1 + \exp[X])$  and  $C = \ln(Q_0 n_1 / Q_1 n_0)$ . Note that, as eq. (36) is valid for any  $W$ , eq. (38) is valid for any  $C$ . The value of  $C$  given below eq. (38) is, however, the one consistent with the optimal choice for  $W$  (eq. (37)). In practical calculations the value of  $C$  is determined graphically.

Writing

$$(39) \quad \langle f(\beta(U_0 - U_1) + C) \rangle_1 = n_1^{-1} \sum_1 f(\beta(U_0 - U_1) + C)$$

and the corresponding expression for  $\langle f(\beta(U_1 - U_0) - C) \rangle_0$ , we obtain from (38)

$$(40a) \quad \beta \Delta F = \ln \frac{\Sigma_1 f(\beta(U_0 - U_1) + C)}{\Sigma_0 f(\beta(U_1 - U_0) - C)} + C - \ln(n_1/n_0),$$

while the condition for the optimal choice of  $C$  can be written as

$$(40b) \quad \beta \Delta F = C - \ln(n_1/n_0).$$

The best estimate for  $\Delta F$  is obtained by choosing  $C$  such that (40a) and (40b) are satisfied simultaneously, which occurs for a value of  $C$ , and that

$$(41) \quad \Sigma_1 f(\beta(U_0 - U_1) + C) = \Sigma_0 f(\beta(U_1 - U_0) - C).$$

Because the optimum value of  $C$  is not known *a priori*, it is useful either to compute  $\Sigma_1$  and  $\Sigma_0$  for a range of  $C$  values during the simulation, or, more conveniently, to store a histogram of potential-energy differences, *i.e.* the functions  $p_0(\Delta U)$  and  $p_1(\Delta U)$  mentioned above, and carry out the solution for the optimal value of  $C$  afterwards. For more details the reader is strongly urged to consult Bennett's very lucid paper [31]. In appendix B we show how the acceptance ratio and overlapping-distribution methods can be generalized to microcanonical simulations.

The acceptance ratio method has been applied by a number of authors [51, 53, 56, 57] and its extension to quantum systems has been discussed by JACUCCI [54].

A few general remarks on the acceptance ratio and overlapping-distribution methods are in place. First of all, both methods can be used simultaneously using the accumulated histograms  $p_0(\Delta U)$  and  $p_1(\Delta U)$ . RAHMAN and JACUCCI [53] have observed that the acceptance ratio method tends to be the more accurate method of the two. Secondly, both methods become less efficient as the number of particles in the system is increased. Large systems must be studied by multistage sampling techniques. The feature that larger is not necessarily better is typical of all techniques discussed in this subsection.

In subsect. 2'7 we shall argue that, for large systems and a fixed number of stages in the multistage sampling, the overlapping-distribution method becomes equivalent to thermodynamic integration.

Finally it is worth pointing out that the acceptance ratio method should provide a better estimate of the chemical potential than Widom's method (subsect. 2'3).

To my knowledge Bennett's acceptance ratio method has not yet been applied to the computation of chemical potentials.

**2'6. Umbrella sampling.** — We mentioned in the previous subsection that, although free-energy differences can in principle be evaluated using an expression

of the form

$$(25) \quad Q_1 = Q_0 \langle \exp [-\beta(U_1 - U_0)] \rangle_0,$$

the applicability of this approach is limited by the fact that, whenever  $U_0$  and  $U_1$  are not very similar, the probability  $f_0(U)$  of sampling a point in the configuration space of system 0 for which  $\exp [-\beta(U_1 - U_0)]$  is appreciable tends to be very small. TORRIE and VALLEAU [6, 58-61] have devised a method to improve the sampling of part of configuration space where the product  $f_0^T(U) \exp [-\beta \Delta U]$  is large by carrying out a biased (non-Boltzmann) sampling.

The basic idea behind this Monte Carlo scheme is that the relative probability to sample a point  $\mathbf{q}^N$  in configuration space is no longer proportional to  $\exp [-\beta U_0(\mathbf{q}^N)]$ , but to  $w(\mathbf{q}^N) \exp [-\beta U_0(\mathbf{q}^N)]$ , where the weighting function  $w$  is chosen such that both the region where  $f_0^T(U)$  is large and the region where  $\exp [-\beta \Delta U] f_0^T(U)$  has its maximum are adequately sampled. The relation between the desired average (eq. (25)) and the average obtained by using the biased sampling is given by

$$(42a) \quad \langle \exp [-\beta \Delta U] \rangle_0 = \frac{\int d\mathbf{q}^N (\exp [-\beta U_0] w) w^{-1} \exp [-\beta \Delta U]}{\int d\mathbf{q}^N (\exp [-\beta U_0] w) w^{-1}}$$

$$(42b) \quad = \frac{\langle \exp [-\beta \Delta U] / w \rangle_w}{\langle 1/w \rangle_w},$$

where the angular brackets with subscript  $w$  indicate an average over the biased random walk. Equation (42b) can be written in a slightly different form, namely

$$(42c) \quad \langle \exp [-\beta \Delta U] \rangle_0 = \langle \exp [-\beta \Delta U] / w \rangle_w \langle w \rangle_0.$$

The latter equation shows most clearly that in order to get reliable results  $w$  should be chosen such that  $w \exp [-\beta U_0]$  is reasonably large in the region of configuration space accessible to system 1 (otherwise the first term on the right-hand side of eq. (42c) vanishes), but  $w$  should also have an appreciable value wherever  $\exp [-\beta U_0]$  is large (otherwise the second right-hand term in (42c) vanishes). The fact that  $w \exp [-\beta U_0]$  is designed to cover both  $f_0^T(U)$  and  $f_1^T(U)$  explains the name «umbrella sampling». This introduction to umbrella sampling is, of course, incomplete without giving the recipe for the weighting function  $w$ . Unfortunately, no general prescription can be given.

Sometimes  $w$  is determined by trial and error, in other cases the function  $w \exp [-\beta U_0]$  corresponds to some intermediate value of the potential-energy function (e.g.,  $w \exp [-\beta U_0] = \exp [-\beta(U_0 + U_1)/2]$ ) and in other cases still physical intuition about  $\gamma_0(U)$  (eq. (27)), the density of states in configuration space as a function of  $U_0$ , is used to choose a form for  $w$  which guarantees as uniform a sampling of the relevant part of configuration space as possible. As the system size becomes larger, it becomes increasingly difficult to find a

weighting function that does the job. In such cases umbrella sampling is combined with multistage sampling. Umbrella sampling (US), or very similar techniques, has been used by a number of authors [24, 25, 44, 45, 58-65]. Umbrella sampling has some advantages and some disadvantages as well. To begin with the latter: US is usually carried out with a «nonphysical» weighting function, as a consequence setting up a US run implies modifying a normal Monte Carlo program. As humans are fallible, this always entails more risks than just gathering some extra statistics in the course of a normal simulation. A second disadvantage, certainly for the less experienced, is the fact the success of the method depends on the choice of  $w$ .

In some cases the choice may be obvious, but often it requires some groping-around in configuration space. On the other hand, there are several advantages associated with the use of umbrella sampling. First of all, given a reasonable choice for  $w$ , free-energy differences (or, for that matter, mechanical quantities) can be obtained for a range of different Hamiltonians and/or temperatures. This was the incentive behind the early work of McDonald and Singer [44-46].

A second advantage is that the US method is actually far more general than suggested by eq. (42). Instead of  $\exp[-\beta\Delta U]$  any other function  $A(\mathbf{q}^N)$  may be probed [58]. Let us, for instance, consider the case that we are interested in the probability that the quantity  $A(\mathbf{q}^N)$  has its value in an interval  $dX$  around  $X$ . We assume that this value of  $A$  is very unlikely in the original ensemble, it could, for instance, correspond to an improbable molecular conformation or a large fluctuation of some order parameter. In that case, simple Boltzmann sampling will yield very poor statistics on the desired probability.

However, with umbrella sampling the weighting function  $w$  can be chosen such that the relevant region of configuration space is adequately sampled.

The probability density to observe  $A$  around  $X$  is then given by

$$(43) \quad P_A(X) = \frac{\langle \delta(A - X)/w \rangle_w}{\langle 1/w \rangle_w}.$$

In this way umbrella sampling can be used to estimate the probability of rare events, or to construct the Landau free energy associated with a particular type of order parameter fluctuations (see sect. 4).

**2.7. Thermodynamic integration.** — Thermodynamic integration (TI) is undoubtedly the method most widely used to compute absolute free energies and free-energy differences. The reason is that, although it may be more time consuming than some of the sophisticated methods described above, it is straightforward, accurate and does not run into special problems at high densities or for large system sizes. Moreover, it is closest to the way free-energy differences are measured in the real world. The simplest TI methods rely on

the fact that the system under study can be expanded, compressed, heated or cooled to a system of known free energy, henceforth referred to as the reference system. The thermodynamic relations used in simple thermodynamic integrations are

$$(44a) \quad (\partial F / \partial V)_{N,T} = -P$$

and

$$(44b) \quad (\partial(F/T) / \partial T^{-1})_{N,V} = E.$$

For example, if one wishes to compute the free energy of a dense fluid, the ideal gas is often taken as the reference state. Using eq. (44a), the free energy of the fluid at a volume  $V$  is written as

$$(45) \quad F(V) = F(V_0) - \int_{V_0}^V P(V') dV',$$

where  $V_0$  is a volume sufficiently large that  $F(V_0)$  may be replaced by  $F_{\text{id}}(V_0)$ , the free energy of an ideal gas at the same density. Equation (45) can be cast in a form that is computationally more convenient. Using  $dV = -N/\rho^2 d\rho$  and the ideal-gas law  $P_{\text{id}} = \rho kT$ , eq. (45) becomes

$$(46) \quad \frac{F(\rho)}{NkT} = \frac{F_{\text{id}}(\rho)}{NkT} + \int_0^{\rho} ((P/\rho' kT - 1)/\rho') d\rho'.$$

The advantage of eq. (46) over eq. (45) is that the former contains two logarithmically diverging contributions which cancel, while the latter contains only well-behaved terms. Note that at low densities the integrand in eq. (46) can be expanded:

$$(47) \quad (P/\rho' kT - 1)/\rho' = B_2 + B_3 \rho' + \dots,$$

where  $B_n$  is the  $n$ -th virial coefficient.

In order to obtain reliable estimates of  $F(\rho)$  from eq. (46), knowledge of  $B_2$  is essential. Knowledge of higher virial coefficients is useful if they happen to be available. (The literature abounds with applications of eq. (46).)

Thermodynamic integration using eq. (44b) is employed in two rather different cases. The first is when the system approaches the reference system as  $T \rightarrow \infty$ . Examples are a hard-core fluid with bounded continuous interaction such as hard spheres with an added soft interaction, or the Lennard-Jones fluid which approaches the soft-sphere ( $r^{-12}$ ) fluid as  $T \rightarrow \infty$ . In either case the free energy at temperature  $T$  of the system under consideration can be

expressed as

$$(48) \quad \frac{F(T)}{T} = \frac{F_{\text{ref}}(T)}{T} - \int_0^{1/T} (E_{\text{ref}}(T') - E(T')) d(1/T').$$

Examples of applications of eq. (48) can be found in [49, 66].

The second application of eq. (45*b*) takes the reference state at  $T=0$ . This method is often employed to compute the free energy of crystalline solids.

The reference state is the harmonic solid. The free-energy integration proceeds as in eq. (48) but for the fact that it is convenient to use  $T'$  instead of  $1/T'$  as integration variable over the range  $0 \leq T' \leq T$ . The harmonic-lattice method was first introduced in this context by HOOVER *et al.* [67, 68]. Other examples of applications can be found in [69-71].

The thermodynamic-integration methods mentioned thus far are all « natural » techniques, in the sense that they can also be carried out in the real world.

In addition to these natural TI methods there is a wide class of « artificial » TI techniques. For the latter the integration variable is a quantity such as the strength of intermolecular interaction that is not normally under the control of the experimentalist. Let us denote this control parameter by  $\lambda$ .

The Hamiltonian of the system under study is now a function  $H(\lambda)$  of  $\lambda$ .

As a consequence the free energy also depends on  $\lambda$ :

$$(49) \quad F(\lambda) = -kT \ln \left( \frac{1}{A^{3N} N!} \int \exp[-\beta U(\lambda)] d\mathbf{q}^N \right).$$

In eq. (49) we have limited ourselves to the case that only the potential energy depends on  $\lambda$ . Parametrizations of the kinetic energy can be handled analytically and are anyway of little interest. The usual procedure is to choose a form for  $U(\lambda)$  such that  $F(\lambda=0)$  is known, while  $F(\lambda=1)$  is the free energy we wish to determine. Then, using the fact that

$$(50) \quad \frac{\partial F(\lambda)}{\partial \lambda} = \frac{\int (\partial U(\lambda)/\partial \lambda) \exp[-\beta U(\lambda)] d\mathbf{q}^N}{\int \exp[-\beta U(\lambda)] d\mathbf{q}^N} = \left\langle \frac{\partial U(\lambda)}{\partial \lambda} \right\rangle_{\lambda},$$

we may obtain  $F(\lambda=1)$  from

$$(51a) \quad F(\lambda=1) = F(\lambda=0) + \int_0^1 d\lambda' \left\langle \frac{\partial U(\lambda')}{\partial \lambda'} \right\rangle_{\lambda'}.$$

Note that  $\langle \partial U/\partial \lambda \rangle_{\lambda}$ , the canonical average of a mechanical quantity  $\partial U/\partial \lambda$  for a system with Hamiltonian  $H(\lambda)$ , can be obtained by computer simulation.

A typical example of eqs. (50), (51) is the situation where  $F$  is known for

a system with potential-energy function  $U_0$  (e.g., a hard-sphere fluid), while we wish to know  $F$  for a potential-energy function  $U_0 + U_1$ . A possible parametrization in this case would be  $U(\lambda) = U_0 + \lambda U_1$ , and eq. (51) would simplify to

$$(51b) \quad F(\lambda = 1) = F(\lambda = 0) + \int d\lambda' \langle U_1 \rangle_{\lambda'}.$$

In practice the thermodynamic integration in eqs. (51a) and (51b) is best performed using an  $n$ -point Gauss-Legendre quadrature [72], with  $n$  typically 5 to 10.

The parametrization of  $U(\lambda)$  will be chosen such that the integrand is a reasonably smooth function of  $\lambda$ . Typical examples of such free-energy calculations can be found in ref. [12, 73-75]. Most other applications will be discussed in the next section on phase transitions. It is interesting to compare thermodynamic integration with Bennett's method of multistage sampling of the potential-energy difference. Suppose that at each quadrature point  $\lambda_i$  of our thermodynamic integration (eq. (51b)) we also compute the distribution function  $p_{\lambda_i}(U_1)$ . Then we can see that the Bennett distribution contains information not just about  $\langle U_1 \rangle_{\lambda}$ , but also about  $\langle U_1^2 \rangle_{\lambda} - \langle U_1 \rangle_{\lambda}^2$  and higher moments, *i.e.* of higher derivatives  $\partial^n F(\lambda)/\partial \lambda^n$ . It might, therefore, seem that Bennett's method is always preferable. This is, however, not necessarily true.

First of all, during a TI run these higher moments could also be computed at no extra cost. But more importantly, as the system size grows, the distribution  $p_{\lambda_i}(U_1)$  tends to become rather narrow. In that case it is to a good approximation a Gaussian which is completely specified by  $\langle U_1 \rangle_{\lambda}$  and  $\langle U_1^2 \rangle_{\lambda} - \langle U_1 \rangle_{\lambda}^2$ . Still it might seem that this contains more information than is used in the integration of eq. (51b). After all, if  $n$  points and  $n$  derivatives of  $\partial F/\partial \lambda$  are given, we can construct a polynomial of degree  $2n - 1$  which fits these data exactly. In contrast, the straightforward thermodynamic integration uses only  $n$  function values. Nevertheless the two methods are equivalent in this limit as long as the  $\lambda_i$  are chosen according to the Gauss-Legendre prescription because an  $n$ -point Gauss-Legendre quadrature integrates any polynomial of degree  $2n - 1$  or less *exactly*. It should be added that almost all other procedures mentioned in the previous subsections do worse than TI for large  $N$ . A notable exception is Widom's particle insertion method and the related GCMC method. However, these techniques tend to become less efficient at high densities. As mentioned at the beginning of this subsection, thermodynamic integration suffers from neither of these drawbacks. Finally it should be added that thermodynamic integration is not limited to the canonical ensemble. It has been applied to the  $NPT$ -ensemble (see next section) in which case one obtains  $(\partial G/\partial \lambda)_{p,T}$ . It could be applied to the grand canonical ensemble, but this is less useful and has, to my knowledge, not been tried. Nor do I know of applications in the microcanonical ensemble in which case the quantity of interest would be

$(\partial S/\partial\lambda)_{E,V}$ . Using the same reasoning as in appendix A, one can show that  $\partial S/\partial\lambda$  is related to a microcanonical ensemble average:

$$(52) \quad (\partial S/\partial\lambda)_{E,V} = - \langle (\partial U/\partial\lambda)/T^* \rangle_{MC},$$

where  $T^*$  is (but for a term of  $O(1/N)$ ) equal to the instantaneous temperature.

### 3. – First-order phase transitions.

**3'1. Preliminary remarks.** – One of the most important applications of free-energy calculations is the location of first-order phase transitions. First-order phase transitions are not easily observed directly in computer simulations because, for the small system sizes concerned, the free energy required to form an interface is nonnegligible. As a consequence it is often possible to overheat or supercool a phase well beyond its point of thermodynamic stability. In fact, to prepare two coexisting phases in a computer simulation requires a considerable amount of time and effort [76-82]. Hence most computer simulations of first-order phase transitions are designed to obtain the temperature, pressure and chemical potential of the pure phases.

The coexistence point is then located by searching for the point where  $T$ ,  $P$  and  $\mu$  of the two phases are equal. In this section we shall briefly discuss the liquid-vapour transition and then proceed to consider first-order transitions involving solids.

**3'2. Liquid-vapour transition.** – To locate the liquid-vapour coexistence point at a given temperature  $T$ , we want to know the pressure and chemical potential along the corresponding liquid and vapour isotherms. The determination of the chemical potential or, equivalently, free energy of the vapour is no problem because, once we know the vapour isotherm, we can use eq. (46) to determine the excess free energy at a density  $\rho$ . Computing the free energy of the liquid is less straightforward. Equation (46) cannot be employed because the integration path from  $\rho = 0$  crosses the two-phase region. Because equilibration times are very long in a two-phase system, it is difficult to obtain accurate values for the pressure. One method to circumvent this problem was devised by HANSEN and VERLET [83]. These authors artificially constrain density fluctuations in the two-phase region. As a consequence full-scale phase separation is suppressed and equilibration is relatively rapid. It is then possible to use eq. (46) to compute the free energy of the liquid phase. In this way the liquid-vapour coexistence curve for a Lennard-Jones system was first mapped out. Other methods have also been used to locate the liquid-vapour coexistence curve. The vapour-liquid coexistence has been investigated using Widom's particle insertion method for the LJ system [29] and for liquid  $\text{Br}_2$  and  $\text{Cl}_2$  [22]. Grand can-

onical MC has been applied to the LJ system [36, 37, 39]. And umbrella sampling was used to investigate both the LJ fluid [58] and a fluid of dipolar hard spheres [60]. In principle the free energy of the dense liquid could also have been determined by performing thermodynamic integration around the critical point. To our knowledge, this has not been done. However, for a different problem integration around a critical point has been carried out, namely in the case of the transition from isotropic fluid to nematic liquid crystal [84]. The isotropic-nematic transition which is normally first order can be suppressed in a strong magnetic field. Hence the free energy of the nematic phase can be computed by performing thermodynamic integration along a path which consists of compression from the dilute gas in a strong field followed by slowly switching off the field at a typical nematic density.

**3.3. Free energy of solids.** – The free energy of the fluid phase can always be obtained by constructing a reversible path to the dilute-gas reference state. In contrast, a dilute gas cannot be compressed or cooled reversibly to form a crystalline solid because in computer simulation the crystalline phase nucleates irreversibly, if at all, from the metastable fluid. Several methods have been developed to link the solid phase by a reversible path to a reference state of known free energy. The most natural method, already mentioned in the previous section, is to take the low-temperature (or high-pressure) harmonic solid as the reference state and use eq. (44b) (or (44a)) to obtain the free energy of the solid at the desired temperature and density. This method was first applied by HOOVER *et al.* [67, 68] to 3D fluids with a repulsive  $r^{-n}$  potential ( $n = 12, 9, 6, 4$ ). Later authors applied the harmonic-lattice method to the 3D one-component plasma [85], pseudopotential «sodium» [70] and the 2D one-component plasma [86], Lennard-Jones system [69] and  $r^{-6}$  system [71]. There are several factors limiting the applicability of the harmonic-lattice method. First of all, its use is restricted to solid phases that can be cooled down or compressed to a harmonic state. This rules out all solids of particles with hard-core interactions, which are never harmonic. Moreover, it cannot be applied to solids that are only stable under conditions where the harmonic description fails (*e.g.*, plastic crystals). It should be emphasized, however, that it is not necessary to prepare the solid under consideration in a thermodynamically stable harmonic state; mechanical stability suffices. A second factor limiting the use of the harmonic-lattice method is of a more mundane nature. Although the amount of work involved in computing the free energy of a harmonic lattice of atoms or ions should not defer anyone from attempting the calculation, the same cannot be said of an arbitrary molecular solid. A more generally applicable method to compute the free energy of solids is the so-called single-occupancy-cell (SOC) method of Hoover and Ree [87]. In the SOC method an artificial reversible path is constructed from the solid phase to the dilute-gas phase. The reference state is in this case not the ideal gas, but a lattice gas with every particle con-

strained to one cell. The cells form a regular lattice with the same symmetry as the solid under consideration. At high densities the centre of every cell coincides with the lattice position of the particle it is designed to hold. In the dense solid phase the presence of the artificial walls is unimportant because the atoms are kept in their place through interaction with their neighbours. But as the SOC solid is expanded, the walls take over and prevent the atoms from diffusing. As a consequence, the SOC solid does not melt. It can be expanded reversibly to low densities where its partition function is known analytically. The SOC method was used by HOOVER and REE to compute the free energy and hence the melting point of the hard-sphere and hard-disk solids [88]. The same method has also been used to find the melting point of 3D systems with a repulsive  $r^{-n}$  potential ( $n = 12$ ) [67, 89, 90], ( $n = 9, 6, 4$ ) [68], the 3D [83] and 2D [91] Lennard-Jones system. The free energy of the SOC hard-sphere system has also been determined by umbrella sampling [59], but the method does not appear to offer any advantages over straightforward thermodynamic integration.

Although the SOC method is quite flexible and easy to use, it does have a few peculiarities which require some care. First of all, at low densities the equation of state of the SOC gas is a nonanalytic function of density:

$$(53) \quad (P_{\text{soc}} - \rho kT)/\rho^2 = b_2 \rho^\alpha + \dots$$

with  $\alpha = 1/D$  for a  $D$ -dimensional space-filling lattice of cells [87] and  $\alpha = (D+1)/D$  for a lattice of touching spherical cells [68];  $b_2$  plays the role of an effective «second virial coefficient». Its value depends on the intermolecular potential and the nature of the lattice of cells [83]. A second and potentially more serious feature of the SOC method, at least in 3D, is that, at the point where the hard-cell walls take over from the intermolecular forces in stabilizing the lattice, the SOC pressure shows a change of slope [67, 88] and possibly even a discontinuity [90]. In other words, the 3D SOC system goes through a second-order or weakly first-order transition. This implies that long simulation runs are needed to obtain reliable values for the pressure near this point because close to an (almost) 2nd-order transition fluctuations in the thermodynamic properties of the system decay slowly. Moreover, the presence of a cusp in the SOC pressure makes it essential to compute the pressure at a fairly large number of state points because the accuracy of most numerical integration procedures deteriorates if the integrand is not smooth. Another approach to compute the free energy of solid phases by thermodynamic integration along an artificial path was recently proposed by FRENKEL and LADD [92]. In this method the Hamiltonian of the solid under consideration is changed reversibly to that of an Einstein crystal with the same structure. The advantage of this particular reference system is that, as it has the same structure and density as the original solid, there is no reason to expect a phase transition

along the integration path. For hard-core systems the parametrization of the Hamiltonian takes the form

$$(54) \quad H(\lambda) = H_{\text{h.c.}} + \lambda k_{\text{max}} \sum_{i=1}^N (\mathbf{r}_i - \mathbf{r}_i^0)^2,$$

where  $H_{\text{h.c.}}$  is the Hamiltonian of the unperturbed hard-core system,  $\mathbf{r}_i - \mathbf{r}_i^0$  is the displacement of particle  $i$  from its lattice site  $\mathbf{r}_i^0$ , and  $k_{\text{max}}$  is the spring constant tying the particles to their lattice sites in the Einstein crystal.  $k_{\text{max}}$  must be chosen sufficiently large that for  $\lambda = 1$  the free energy of the system approaches that of a true Einstein crystal. The advantage of the method is that it is simple to use and that, with moderate expenditure of computer time, the estimated error in the excess free energy of the solid can be reduced to  $\sim 0.002 NkT$ . In ref. [92] the method is applied to the h.c.p. and f.c.c. phases of hard spheres. The Einstein crystal method has been extended to molecular hard-core systems [84]. The only difference is that in addition to the spring constants fixing the molecular centre-of-mass positions there are now also springs fixing the molecular orientation. Using this approach it has proved possible to determine the melting point of hard ellipsoids of revolution over a wide range of length-to-breadth ratios [84] (see fig. 5). The generalization to systems with a continuous intermolecular potential is straightforward. The

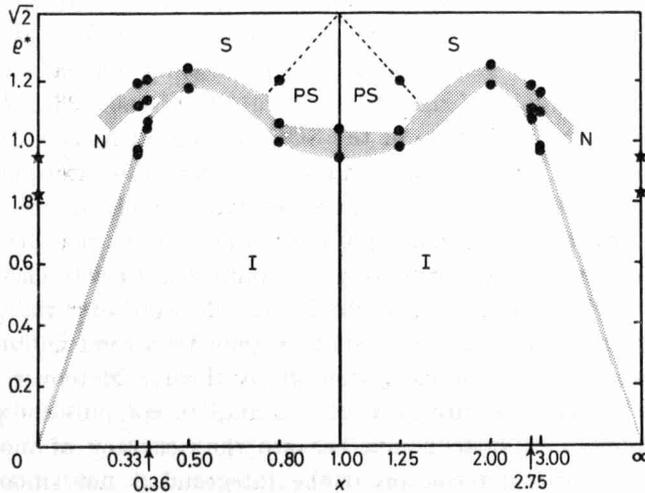


Fig. 5. - Phase diagram of hard ellipsoids of revolution as a function of the length-to-breadth ratio  $X$ . The maximum density  $\sigma = \sqrt{2}$  corresponds to regular close packing. I = isotropic fluid, N = nematic fluid, S = ordered solid and PS = plastic (orientationally disordered) solid. The shaded area is the two-phase region. All points are coexistence points that follow from absolute free-energy computations of the solid and fluid phases (see ref. [84]).

parametrized potential-energy function now becomes

$$(55) \quad V(\lambda) = V_0 + (1 - \lambda)(V_s(\mathbf{q}^N) - V_0) + \lambda k_{\max} \sum (\mathbf{r}_i - \mathbf{r}_i^0)^2,$$

where  $V_0$  is the static lattice energy of the solid and  $V_s(\mathbf{q}^N)$  the potential energy of a given lattice configuration. It is advisable to choose  $k_{\max}$  such that the mean square displacement of the particles varies little as  $\lambda$  is changed. As an example we apply this method to the relative stability of the f.c.c. and b.c.c. phases of a model for helium [55, 93]. In fig. 6 we show the value of  $\langle \partial H(\lambda) / \partial \lambda \rangle_\lambda$

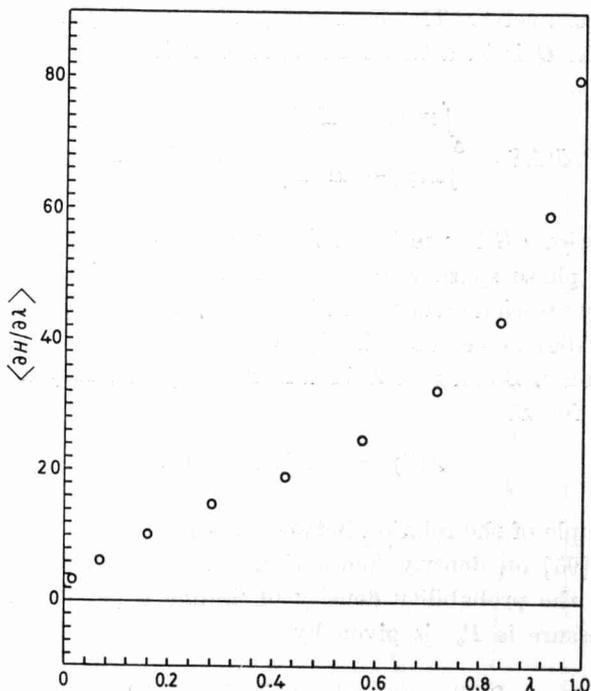


Fig. 6. - Integrand in the free-energy integration from f.c.c. «helium» (see text) to the corresponding Einstein crystal, as a function of the coupling parameter  $\lambda$ . The integrand was evaluated at values of  $\lambda$  corresponding to a 10-point Gauss-Legendre quadrature.

for a number of  $\lambda$  values, for both f.c.c. and b.c.c. «helium» at a reduced temperature of  $T^* = 32$  (in units  $\epsilon_{LJ} = 10.22 k$ ) and a reduced density  $\rho^* = 2.41$ . At this density and temperature the f.c.c. phase is still marginally more stable than the b.c.c. phase ( $\Delta F = (F_{\text{b.c.c.}} - F_{\text{f.c.c.}}) / N_k T = 0.0087 \pm 0.0018$ ). For more details on the Einstein crystal method we refer the reader to [94]. We wish to remind the reader that thermodynamic integration and multistage

sampling are closely related. An example of the application of multistage sampling to compute the free-energy difference of the f.c.c. and b.c.c. phases for a number of model potentials can be found in [53].

#### 4. - Free energy of fluctuations.

Thus far we have been concerned with the computation of the free energy of bulk phases. Now we wish to make a few remarks about the free energy associated with fluctuations. Consider a mechanical quantity  $S(\mathbf{q}^N)$  which in principle may be anything, but in cases of practical interest usually is some kind of order parameter. The probability of observing an equilibrium fluctuation such that  $O$  is in a range  $\Delta O$  around  $O$  is

$$(56) \quad P(S)\Delta S = \frac{\int \exp[-\beta H] d\mathbf{q}^N}{\int \exp[-\beta H] d\mathbf{q}^N} \equiv \exp[-\beta F(S)]\Delta S,$$

where the subscript  $\Delta S$  in the integral in the numerator restricts the integral to that part of phase space where  $O$  is within the specified range.

The second expression on the right in eq. (56) defines the free-energy density  $F(S)$ . From eq. (56) we see that the free-energy density associated with a particular fluctuation of  $S$  can be obtained from the probability density of finding a certain value for  $S$ :

$$(57) \quad F(S) = -kT \ln (P(S)).$$

A classical example of the relation between  $F(S)$  and  $P(S)$  can be found in the work of Wood [95] on density fluctuations in the isobaric ensemble.

In this case the probability density of finding a particular value of  $V$ , if the applied pressure is  $P_0$ , is given by

$$(58) \quad P(V) = c \exp[-\beta(P_0 V + F(V))],$$

where  $c$  is a normalizing constant. The term  $P_0 V + F(V)$  plays the role of the free enthalpy  $G(V)$  associated with a given fluctuation of  $V$ . We see that  $G$  has its minimum if

$$(59) \quad -(\partial F/\partial V) = P_0.$$

Equation (59) expresses just the condition for mechanical equilibrium. Wood observed that eq. (58) offers the possibility of probing the equation of state at densities around the equilibrium density given by eq. (59). A similar relation exists between the probability density of potential-energy fluctuations in the canonical ensemble and the dependence of  $U$  on  $T$ .

PARRINELLO [96] has recently pointed out that the probability density of the scaling parameter  $s$  in Nosé's canonical MD [97] contains comparable information. An interesting feature of eq. (58) is the fact that, in principle, at a first-order phase transition  $P(V)$  becomes double peaked.

The pressure for which the two peaks of  $P(V)$  have equal height is the coexistence pressure because at that point two different volumes  $V_1$  and  $V_2$  satisfy the relation  $\partial F/\partial V = -P_0$  and  $G(V_1) = G(V_2)$ . Unfortunately, this property of  $P(V)$  can only be exploited for very small systems. For larger systems configuration space is not adequately sampled on the time scale of a simulation and hence we do not obtain the correct  $P(V)$ . However, in other situations, in particular near weakly first-order or higher-order phase transitions eq. (57) may be extremely useful to study precursor effects of the transition. One way of analysing such precursor effects is in terms of the Landau free energy, the expansion of the free-energy density in integer powers of the order

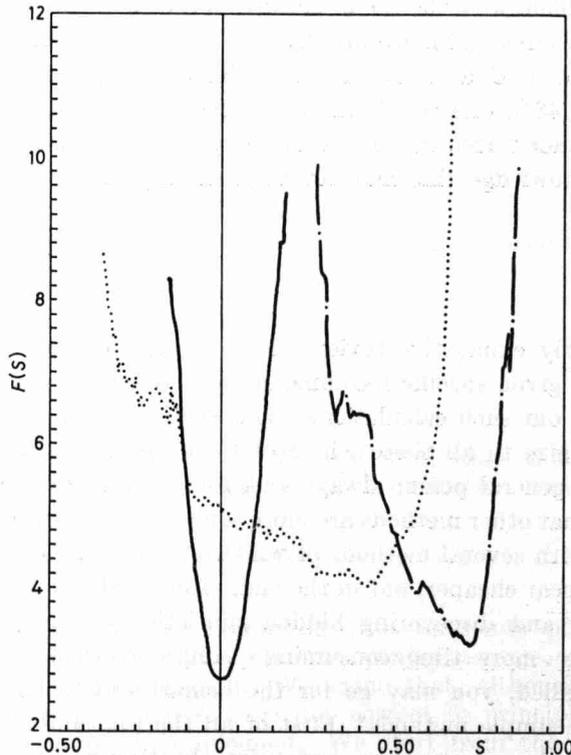


Fig. 7. - The Landau free energy (in units  $kT$ ) associated with fluctuations of the nematic order parameter  $S$  in a system of 100 hard platelets of diameter  $\sigma$  (ref. [23]). Drawn curve: low density, well into the isotropic fluid phase. Dotted curve: higher density, just beyond the isotropic nematic transition; note that the most probable value of  $S$  has moved to a nonzero value. Dash-dotted curve: high density, well inside the nematic phase; only small fluctuations around a nonzero order parameter are possible.

parameter:

$$(60) \quad F(S) = F_0 + aS^2 + bS^3 + cS^4 + \dots$$

Of course, an expansion of this type need not be correct and indeed, close to phase transitions, the simple Landau picture often fails. The important point we wish to stress here is that the Landau free energy is not just an abstract concept that may or may not be useful. Using eq. (57) the Landau free energy can be « measured » in a computer simulation. As an example, fig. 7 shows the Landau free energy associated with fluctuations of the orientational order parameter  $S$  close to the (weakly first-order) transition from isotropic liquid to nematic liquid crystal. The fact that  $P(S)$  in fig. 7 develops a double-peaked structure confirms the first-order nature of the transition. Actually, in this particular case the Landau expansion eq. (60) appears to run into trouble. For further details see ref. [23].

One basic problem with the use of eq. (57) is that  $P(S)$  becomes very narrow for larger system sizes, until eventually the only information one obtains is the average value of  $O$  and its variance. However, as already indicated in subsect. 2'5 (eq. (43)), one could still probe the wings of the distribution, and thereby higher-order terms in the Landau expansion, by using umbrella sampling. To my knowledge this has not been attempted.

## 5. – Conclusions.

After this fairly exhaustive review of free-energy computation techniques I wish to end by given specific recommendations to the newcomer who is considering carrying out such calculations. This section has inevitably a personal bias and I apologize to all those who feel I am giving bad advice.

First of all a general point: always look for the simplest method available even if you feel that other methods are more sophisticated. In general a problem can be tackled with several methods of which at least one is « simple ». Other methods may appear cheaper, but in the end, after all the hours spent programming, debugging and discovering hidden subtleties you may wish you had started with the « more time consuming » simple method. Of course, once you are more skilled, you may go for the « smart » methods.

What are the simple methods? First of all the « natural » thermodynamic-integration methods, compression, expansion, heating or cooling. Remember, if you have a working MD or MC program, you can do it. Of these the methods that have the harmonic lattice as their reference point are less favoured unless the harmonic-crystal free energy can easily be calculated. For solids, the Einstein crystal method (personal bias!) is simplest, directly followed by the single-occupancy-cell method. Note that the free-energy difference between two solids can be computed by thermodynamic integration or by Bennett's

acceptance ratio or overlapping-distribution method. All three are easy. The best is to accumulate a histogram of potential-energy differences during the simulations, and use it to try out all three methods. Note that for thermodynamic integration it is advisable to choose values of the coupling parameter  $\lambda$  according to a Gauss-Legendre or similar quadrature. For Bennett's method there is no need to choose the number of points in advance. Start with simulations for  $\lambda = 0$  and  $\lambda = 1$  and keep on doing simulations at intermediate values of  $\lambda$  until you find you have reached the desired accuracy.

If you are studying multicomponent mixtures at low densities use Bennett's modification of the Widom/Shing-Gubbins method or grand canonical MC (but watch your random-number generator!). At higher densities multicomponent systems become difficult and you will probably need one of the « smart » methods. Of the smart methods umbrella sampling seems the most powerful. This method requires some skill, so use it only where the simpler methods will not do. It turns out that there remains a large class of problems where such biased sampling is the only tool available.

\* \* \*

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Figure 1 was drawn by N. D'OLVEYRA. I am grateful for her artwork.

## APPENDIX A

It has been suggested in the literature [29] that the particle insertion method may also be used in microcanonical simulation using

$$(A.1) \quad \beta\mu_{\text{ox}} = -\ln \langle \exp[-V_A/kT'] \rangle,$$

where  $V_A$  is, as before, the interaction of a randomly placed test particle with the other molecules, and  $T'$  is the *running average* of the temperature during microcanonical simulation. We argue that, although this recipe may work satisfactorily in practice, it is not correct in principle. Moreover, the correct recipe is simple to implement. We start from the relation

$$(A.2) \quad dS = dE/T + (P/T) dV - (\mu/T) dN$$

from which it follows that

$$(A.3) \quad -(\mu/T) = \left( \frac{\partial S}{\partial N} \right)_{E,V}.$$

The classical expression for  $S(E, V, N) = k \ln \omega(E)$  is

$$(A.4) \quad S = k \ln \left( \frac{1}{h^{3N} N!} \int \delta(\mathbf{H}_N - E) d\mathbf{p}^N d\mathbf{q}^N \right),$$

where  $\mathbf{H}_N(\mathbf{p}^N, \mathbf{q}^N) = \mathbf{V}(\mathbf{q}^N) + K(\mathbf{p}^N)$  is the Hamiltonian of the system. For simplicity we have assumed that we are dealing with atoms. Generalization to molecules is straightforward. We now write  $(\partial S / \partial N)_{E, V}$  as

$$(A.5) \quad (\partial S / \partial N)_{E, V} \underset{N \rightarrow \infty}{=} k \ln (\omega_N(E) / \omega_{N-1}(E)).$$

Or, introducing  $\varepsilon_N$ , the kinetic energy of the test particle, and  $V_A$ , its interaction with the rest of the system,

$$(A.6) \quad \frac{\omega_N(E)}{\omega_{N-1}(E)} = \frac{1}{h^3 N} \frac{\int \delta(\mathbf{H}_{N-1} + V_A + \varepsilon_N - E) d\mathbf{p}^N d\mathbf{q}^N}{\int \delta(\mathbf{H}_{N-1} - E) d\mathbf{p}^{N-1} d\mathbf{q}^{N-1}}.$$

Using the fact that

$$(A.7) \quad d\mathbf{p}^N = \{(2\pi m)^{3/2(N-1)} / \Gamma(3/2(N-1))\} K^{3/2(N-1)-1} dK$$

(for a system that does not conserve linear momentum, all  $N-1$  should be replaced by  $N$ ), we can readily perform the integrations over the momenta in eq. (A.6):

$$(A.8) \quad \omega_N(E) / \omega_{N-1}(E) = \frac{1}{h^3 N} \frac{\int (E - V_{N-1} - V_A)^{3/2(N-1)-1} (2\pi m)^{\frac{3}{2}} (3/2(N-2))^{-\frac{3}{2}} d\mathbf{q}^N}{\int (E - V_{N-1})^{3/2(N-2)-1} d\mathbf{q}^{N-1}}.$$

Noting that  $E - V_{N-1} = K_{N-1}$ , the kinetic energy in the  $N-1$  particle system, we obtain

$$(A.8') \quad \omega_N(E) / \omega_{N-1}(E) = \left( \frac{2\pi m}{h^2} \right)^{\frac{3}{2}} \cdot \frac{\int (1 - V_A / K_{N-1})^{3/2(N-1)-1} (K_{N-1} / 3/2(N-2))^{\frac{3}{2}} K_{N-1}^{3/2(N-2)-1} d\mathbf{q}^N}{\int (E - V_{N-1})^{3/2(N-2)-1} d\mathbf{q}^{N-1}}.$$

Equation (A.8') can be expressed as a microcanonical expectation value:

$$(A.9) \quad \frac{\omega_N(E)}{\omega_{N-1}(E)} = \left( \frac{2\pi m}{h^2} \right)^{\frac{3}{2}} \frac{V}{N} \frac{1}{V} \int d\mathbf{q}^N \langle (1 - V_A / K_{N-1})^{3/2(N-1)-1} (K_{N-1} / 3/2(N-2))^{\frac{3}{2}} \rangle_{\text{MC}}.$$

For sufficiently large  $N$  we can write  $(1 - V_A / K_{N-1})^{3/2(N-1)-1}$  as

$$\exp \left[ -V_A / \left( K_{N-1} / (3/2(N-2) + \frac{1}{2}) \right) \right].$$

With the conventional definition of the instantaneous temperature  $T_i$

$$(A.10) \quad T_i = K_{N-1} / (3/2(N-2)k)$$

and neglecting corrections of order  $N^{-1}$  to  $T_1$ , we obtain

$$(A.11) \quad \omega_N(\mathbf{E})/\omega_{N-1}(\mathbf{E}) = (\rho A^3)^{-1} \langle T \rangle^{-3} \frac{1}{V} \int d\mathbf{q}_N \langle \exp[-V_A/kT_1] T_1^3 \rangle_{\text{MC}}$$

and finally

$$(A.12) \quad \beta\mu_{\text{ex}} = -\ln \{ \langle T \rangle^{-3} \langle \exp[-V_A/kT_1] T_1^3 \rangle \}.$$

The angular brackets now stand for microcanonical averaging over the phase space co-ordinates of the  $N-1$  particles in the original system for random positions of the test particle. Note that eq. (A.11) can easily be implemented in a molecular-dynamics program because the instantaneous temperature is always well defined. Note also that, because of the convexity of  $\exp[-V_A/T_1] T_1^3$ , eq. (A.11) must lead to a *lower* estimate of  $\mu_{\text{ex}}$  than is obtained by the method of ref. [29]. This may be serious for small systems or for systems with a large heat capacity (large  $T$  fluctuations). Note that the  $\mu$ 's in ref. [29] tend to be marginally higher than earlier data. For molecular systems the  $(T_1/\langle T \rangle)^3$  is replaced by some other power of  $T_1/\langle T \rangle$ , e.g. 5/2 for linear molecules.

## APPENDIX B

Bennett's acceptance ratio method and the method of overlapping distributions can be generalized to the microcanonical ensemble. In the literature it has thus far been assumed [53] that Bennett's canonical expressions can be used without modification in microcanonical simulations. Here we argue that, although such an approach may yield reasonable answers for large systems, it is not correct. This is important because free-energy difference calculations are often carried out on rather small systems where the choice of the ensemble does make a difference.

As in appendix A, the central quantity to be computed in a microcanonical simulation is the entropy difference between two systems. The expression for the entropy of a classical  $N$ -particle system with total energy  $E$  is

$$(B.1) \quad S = k \ln (\omega(E)) = k \ln \left\{ (h^{3N} N!)^{-1} \int \delta(\mathbf{H}_N - E) d\mathbf{p}^N d\mathbf{q}^N \right\}.$$

Performing the integration over momenta, we obtain

$$(B.2) \quad \omega(E) = c \int (E - U(\mathbf{q}^N))^{(3N-5)/2} d\mathbf{q}^N,$$

with  $c = \{(2\pi m)^{(3N-5)/2} / \Gamma((3N-3)/2)\} / h^{3N} N!$ . As in appendix A we have assumed that we are dealing with an atomic system and that linear momentum is conserved. The entropy difference between two  $N$ -particle systems 0 and 1 is given by

$$(B.3) \quad \Delta S = k \ln (\omega_1(E_1)/\omega_0(E_0)) = k \ln \frac{\int (E_1 - U_1(\mathbf{q}^N))^{(3N-5)/2} d\mathbf{q}^N}{\int (E_0 - U_0(\mathbf{q}^N))^{(3N-5)/2} d\mathbf{q}^N}.$$

Starting from eq. (B.3), we can easily derive the microcanonical equivalent of the overlapping-distribution and acceptance ratio methods.

I) *Overlapping-distribution method.* Let us denote the kinetic energy of systems 0 and 1 by  $K_0 = E_0 - U_0(\mathbf{q}^N)$  and  $K_1 = E_1 - U_1(\mathbf{q}^N)$ . Note that  $K_0$  and  $K_1$  are explicit functions of the particle co-ordinates  $\mathbf{q}^N$ . Consider the probability of observing the quantity  $x = ((3N - 5)/2) \ln (K_1/K_0)$  in a range  $dx$  around  $x$ . If microcanonical sampling is carried out in system 0, the expression for the probability density  $p_0(x)$  of  $x$  is

$$(B.4) \quad p_0(x) = \frac{\int \delta\{((3N - 5)/2) \ln (K_1/K_0) - x\} K_0^{(3N-5)/2} d\mathbf{q}^N}{\int K_0^{(3N-5)/2} d\mathbf{q}^N}.$$

Using eq. (B.3), (B.4) can be rewritten as

$$(B.5) \quad p_0(x) = \exp [\Delta S/k] \frac{\int \delta\{((3N - 5)/2) \ln (K_1/K_0) - x\} \exp [-x] K_1^{(3N-5)/2} d\mathbf{q}^N}{\int K_1^{(3N-5)/2} d\mathbf{q}^N}$$

or

$$(B.6) \quad p_0(x) = \exp [\Delta S/k] \exp [-x] p_1(x).$$

Note that eq. (B.6) is of the same form as eq. (32). For  $|K_1 - K_0| \ll K_0$  we can write

$$(B.7) \quad ((3N - 5)/2) \ln (K_1/K_0) \simeq (\Delta E - \Delta U)/kT_0^*,$$

where  $T_0^*$  is the *instantaneous* temperature of system 0. In the special case that the average temperatures of 0 and 1 are equal we can combine (B.6) and (B.7) to yield

$$(B.8) \quad p_0((\Delta E - \Delta U)/kT_0^* = x) = \exp [\Delta S/k] \exp [-x] p_1((\Delta E - \Delta U)/kT_1^* = x),$$

or, with  $x' = x - \Delta E/kT$ , where  $T$  is the average of  $T_1^*$  and  $T_0^*$ ,

$$(B.9) \quad p_0(\{\Delta E(1/kT_0^* - 1/kT) - \Delta U/kT_0^*\} = x') = \exp [-\Delta F/kT] \exp [-x'] p_1(\{\Delta E(1/kT_1^* - 1/kT) - \Delta U/kT_1^*\} = x').$$

Note that eq. (B.9) is similar, but not identical, to eq. (32). The difference is due to the effect of temperature fluctuations in the microcanonical ensemble. Of course, in the thermodynamic limit this effect disappears, but in that same limit the overlapping-distribution method loses its advantage over thermodynamic integration.

II) *Acceptance ratio method.* To arrive at the microcanonical equivalent of Bennett's acceptance ratio method we start, once more, from eq. (B.3).

We begin with the identity

$$(B.10) \quad \frac{\omega_1(\mathcal{E}_1)}{\omega_0(\mathcal{E}_0)} = \frac{\omega_1(\mathcal{E}_1) \int W(\mathbf{q}^N) (K_1 K_0)^{(3N-5)/2} d\mathbf{q}^N}{\omega_0(\mathcal{E}_0) \int W(\mathbf{q}^N) (K_1 K_0)^{(3N-5)/2} d\mathbf{q}^N},$$

where  $W(\mathbf{q}^N)$  is an as yet still arbitrary function. Proceeding exactly as in ref. [31] it is easy to show that the estimated error in  $\Delta S$  is minimized for the following choice of  $W(\mathbf{q}^N)$ :

$$(B.11) \quad W(\mathbf{q}^N) = \text{const} \cdot X \{ (\omega_0(\mathcal{E}_0)/n_0) K_1^{(3N-5)/2} + (\omega_1(\mathcal{E}_1)/n_1) K_0^{(3N-5)/2} \}^{-1}.$$

Here  $n_0$  and  $n_1$  are the numbers of independent configurations sampled in a microcanonical simulation of systems 0 and 1, respectively. Defining, as in eq. (B.4), a quantity  $x$  by

$$(B.12) \quad x = \{(3N - 5)/2\} \ln (K_1/K_0),$$

we can combine eqs. (B.10) and (B.11) to yield

$$(B.13) \quad \frac{\omega_1}{\omega_0} = \frac{\langle f(-x + C) \rangle_0}{\langle f(+x - C) \rangle_1} \exp [C],$$

where the angular brackets stand for a microcanonical average in system 0 or 1,  $f(y) \equiv (1 + \exp [y])^{-1}$  is the Fermi function, and  $C$  is a constant. Although eq. (B.13) is in principle valid for any value of  $C$ , the best estimate for  $\Delta S$  results for the choice

$$(B.14) \quad C = \ln \{ (\omega_1/n_1) (n_0/\omega_0) \}.$$

If  $|K_1 - K_0| \ll K_0$  we can, as in eq. (B.7), replace  $x$  by  $(\Delta E - \Delta U)/kT^*$ , with  $T^*$  the instantaneous temperature. In the special case that  $\langle T_1^* \rangle = \langle T_0^* \rangle = T$ , we can rewrite eq. (B.13) as

$$(B.15) \quad \exp[-\Delta F/kT] = \frac{\langle f(-\Delta E(1/kT_0^* - 1/kT) + \Delta U/kT_0^* + C') \rangle_0}{\langle f(+\Delta E(1/kT_1^* - 1/kT) - \Delta U/kT_1^* - C') \rangle_1} \exp [C'],$$

with  $C' = C - \Delta E/kT$ . Note that eq. (B.15) is similar to the canonical expression (eq. (38)), but, as with the overlapping-distribution case, the microcanonical term is changed due to temperature fluctuations.

It should be stressed that the microcanonical methods described above are just as easily implemented in a normal MD program as the less appropriate canonical expressions. The best approach is to accumulate a histogram of  $\ln \{ (\mathcal{E}_1 - U_1) / (\mathcal{E}_0 - U_0) \}$  during simulations of systems 0 and 1. The analysis required to solve eq. (B.6) or eqs. (B.13) and (B.14) then proceeds exactly as with the original Bennett methods and can be carried out afterwards. Extension of the microcanonical methods to multistage sampling is straightforward.

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