Calculation of free energies of Lennard-Jones crystals via molecular dynamics

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The effectiveness of the determinant method and of energy distribution methods for the calculation of free energies with molecular dynamics sampling in the isothermal–isobaric ensemble has been demonstrated. The accuracy of the methods employed has been characterized. The quasiharmonic and anharmonic free energies of two-dimensional and three-dimensional crystals have been estimated over a wide range of temperatures.

I. INTRODUCTION

Most molecular dynamics simulation to date have concentrated on calculating mechanical thermodynamic properties by averaging those properties which are defined in terms of instantaneous coordinates and/or velocities over the trajectories. Entropy, however, is a collective property and can only be determined by evaluating the partition function of the model system. Computation of the vibrational contribution to the entropy has been attempted by evaluating the phonon spectrum[1]; but so far, molecular dynamics lacks easy to use semidirect or direct techniques to access entropy and free energies.

The constraint of constant volume in standard molecular dynamics in the canonical ensemble has been recently removed allowing the possibility of simulating periodic cells of fluctuating volume and shape. Molecular dynamics in the isothermal–isostress ensemble is based on an extension by Parrinello and Rahman[2] of a Lagrangian formulation due to Andersen[3] for a system with flexible borders. In this formulation the coordinates of the edges of the simulation cell are dynamical variables. The volume and shape of the simulation cell are free to vary to accommodate the imbalance between an externally applied stress and the internal stress. Three methods originally developed for the Monte Carlo algorithm have been employed with the flexible borders formulation of molecular dynamics to compute the absolute free energy, the free energy difference of two systems at the same temperature, or the free energy difference of the same system at two different temperatures of Lennard-Jones systems.

The first technique used to compute absolute Helmholtz free energies is due to Hoover.[4] The classical canonical partition function can be evaluated at low temperatures, in the quasiharmonic approximation. The partition function is inversely proportional to the square root of the determinant of a matrix built from the force constant coefficients matrix by fixing particle 1 at the origin. The proportionality constant is a function of the temperature, the volume, the number of particles, and the static lattice potential energy. The force constant coefficients are evaluated at the equilibrium positions from an average structure generated in a molecular dynamics run. The determinants of big matrices are efficiently computed with the lower–upper method. The determinant technique has limitations intrinsic to the quasihar-

monic approximation. The quasiharmonic approximation is valid only at low temperature.[5] It gives only the vibrational contribution to the free energy and is effective only in temperature ranges where reliable average structures are accessible. On the other hand, at very low temperatures, the energy levels are quantized, the classical form of the canonical partition function is not useful anymore, and quantum corrections have to be taken into account.[6]

The second set of methods are the energy distribution methods. These methods were first introduced by Valleau et al.[7] and Bennett.[8] The heart of the energy distribution methods is that one is able to express ratios of partition functions between a system of interest and a reference system without knowing the partition functions themselves. The reference system may differ from the system of interest not only in its thermodynamic state variables but also in its Hamiltonian. The former can give the free energy difference for the same system at two temperatures; the latter, the free energy difference of two systems at the same temperature. Because of their similarity to calorimetry, these methods are sometimes called computer calorimetry. The distributions of enthalpy for the former method or the distributions of the difference in enthalpy of the reference system and of the system studied for the latter, which are needed for the calculation of the ratios of partition functions in the isothermal–isobaric ensemble, are generated as part of the main loop in a molecular dynamics simulation. The energy distribution methods when applied to systems in the (N,P,T) ensemble will, therefore, yield differences in Gibbs free energies.

II. RESULTS AND DISCUSSION

A. Energy distribution technique with different Hamiltonians

We have calculated the free energies of a large set of close-packed two-dimensional systems. The energy distribution technique for systems having different Hamiltonians was applied to perfect crystals with 52 and 104 particles interacting through a Lennard-Jones (12-6) potential. The Lennard-Jones potential was truncated between the first and second nearest neighbors (range of interaction $R_i = 1.5\sigma$). The interatomic potential of the reference system was chosen to be a Hooke's law type potential:

$$\phi_0(r) = (\epsilon/\omega^2)\{r - (\sigma + \omega)\}^2 - \epsilon$$

$$[\text{with } \omega = (2^{1/6} - 1)\sigma] ,$$

where ϵ and σ are the Lennard-Jones parameters. This interatomic potential is chosen such that the total potential energy function had a quadratic form and the system did not show any anharmonic contribution to its entropy. The determinant technique should then give the exact free energy. The determinant technique was also applied to the Lennard-Jones systems. The MD simulations lasted 5000 time steps; a step being 0.002ζ where the characteristic time $\zeta = 2.156 \times 10^{-12}$ s. The distributions of the quantity $(H_0 - H_1)$ generated with the Lennard-Jones interatomic potential as well as with the Hooke's law type potential did not overlap. The gap between the histograms was smaller than the width of the histograms. The discrete histograms were smoothed out empirically with good agreement by an inverse Gaussian distribution which is given by

$$h(x) = (\lambda/2\pi x^3)^{1/2}\exp\{-\lambda(x - \mu)^2/(2\mu^2 x)\} ,$$

where $\mu = \langle H_0 - H_1 \rangle$ and $\lambda = (\mu^3/\sigma^2_{H_0 - H_1})$. This fit allowed us to use the interpolation technique suggested by Bennett[8] when the distributions do not overlap. The calculated thermodynamic data are collected in Table I. The computational conditions were far from being ideal with short simulations and discontinuous, nonoverlapping distributions. The extrapolation technique gives, however, Gibbs free energies within less than $0.06 \, NkT$ for the worst case and typically within less than $0.04 \, NkT$ of the results obtained by the determinant technique. In the range of temperatures $0.055 < T^* < 0.065$, the determinant technique is at its best even for the LJ systems. This temperature is high enough to avoid quantum corrections to the partition function and low enough for anharmonic effects to be negligible. The difference in the two sets of free energies does not reflect the difference in the physical nature of the two techniques which are employed but results from the statistical errors which are associated with both of them. Statistical errors in the free

energy obtained by the determinant technique will arise from deviations in the averaged atomic positions from the equilibrium positions. The offset of the average atomic positions from the equilibrium positions will affect the value of the force constant coefficients and, accordingly, the determinant of the force constant matrix. The static lattice potential energy will also be affected by the distortions from the equilibrium positions. To improve the technique, one should run longer simulations for a better averaging of the atomic coordinates, especially at relatively high temperatures. An alternative method for the generation of a better equilibrium structure is to conduct the simulation with damped equations of motion.[9] The computer calorimetry with two Hamiltonians suffers in precision because of the empirical fitting of the distributions to an inverse Gaussian and the use of the interpolation technique. The width of the distributions decreased from the crystal containing 52 particles to the crystal containing 104 particles but an increase in relative free energy difference with the number of particles was not noticeable.

B. The energy distribution technique at two temperatures

This technique was tested on a 2D perfect crystal containing 104 particles interacting through a Lennard-Jones potential truncated between second and third nearest neighbors (range of interaction $R_i = 2.1\sigma$). A series of MD simulations with flexible borders was conducted in a wide range of temperatures; from $T^* = 0.055$ up to the melting point. Each simulation lasted 10 000 time steps, where each time step equals 4.31×10^{-15} s. For every temperature an average structure and a distribution of enthalpy were generated and the free energies computed by the determinant and the computer calorimetry techniques. A Gaussian distribution was employed to fit the discontinuous enthalpic histograms. The trajectories of the particles are approximately distributed as a Gaussian.[10] Therefore, by the central limit theorem, if the

TABLE I. Thermodynamic data of 2D crystals calculated by molecular dynamics, the determinant technique (DET), and computer calorimetry of systems differing by their Hamiltonians (CC). The interatomic potentials (PO): Hooke's law type (h) and Lennard-Jones (LJ) were truncated between first and second nearest neighbors. N is the number of particles contained in the simulation cell. GEO stands for the approximate geometry of the 2D systems expressed as approximate width of the simulation cell by the approximate height of the simulation cell. The length of the edges of the simulation cell are in reduced units $1^* = 1/\sigma$. The crystals are simulated under a reduced isostatic pressure $P^* = P\sigma^2/4k\epsilon = 0.4936$. The reduced temperatures and energy are related to the temperature and energy by $T^* = T/4\epsilon$ and $E^* = E/4\kappa\epsilon$. The standard error on the Gibbs free energy, ΔG, is given in units of NkT.

N	GEO	PO	T^*	V^*/N	H^*/N	DET S^*/N	DET F^*/N	DET G^*/N	CC S^*/N	CC F^*/N	CC G^*/N	ΔG
52	8×7	h	0.055	1.071	−0.1036	0.10	−0.638	−0.109	⋯	⋯	⋯	
52	8×7	h	0.060	1.071	−0.0941	0.26	−0.638	−0.110	⋯	⋯	⋯	
52	8×7	h	0.065	1.071	−0.0834	0.44	−0.640	−0.111	⋯	⋯	⋯	
52	8×7	LJ	0.055	1.089	−0.1024	0.86	−0.687	−0.149	0.88	−0.689	−0.151	0.04
52	8×7	LJ	0.060	1.093	−0.0912	1.05	−0.694	−0.154	1.09	−0.696	−0.157	0.05
52	8×7	LJ	0.065	1.098	−0.0766	1.24	−0.699	−0.157	1.31	−0.703	−0.161	0.06
104	8×14	h	0.055	1.071	−0.1053	0.19	−0.644	−0.115	⋯	⋯	⋯	
104	8×14	h	0.065	1.071	−0.0827	0.57	−0.648	−0.120	⋯	⋯	⋯	
104	8×14	LJ	0.055	1.090	−0.1022	0.97	−0.693	−0.156	0.93	−0.691	−0.154	0.04
104	8×14	LJ	0.060	1.092	−0.0921	1.18	−0.702	−0.163	1.16	−0.701	−0.162	0.02
104	8×14	LJ	0.065	1.097	−0.0789	1.39	−0.711	−0.169	1.38	−0.710	−0.169	0.00
104	4×28	h	0.055	1.071	−0.1030	0.28	−0.647	−0.118	⋯	⋯	⋯	
104	4×28	LJ	0.055	1.090	−0.1013	1.02	−0.695	−0.157	1.05	−0.697	−0.159	0.04

number of particles is big enough, the distribution of enthalpies is, to first approximation, also a Gaussian.[11] The starting point for the energy distribution technique was the free energy calculated by the determinant technique at $T^* = 0.055$ and we used only computer calorimetric free energies as references for the successive temperatures. The temperature intervals were small enough such that one lay in the limit of overlapping distributions and the quantity: $\{G(T_1)/T_1] - [G(T_0)/T_0]\}$ was systematically calculated at the point $x = (\bar{H}_1 + \bar{H}_0)/2$ where one expects h_1/h_0 to be close to 1, in order to stay as far as possible from the tails of the distributions. The determinant technique worked for temperatures up to 85% of the melting point and the data are given in Table II and Fig. 1. At high temperatures we observed a spontaneous generation of defects which prevented the computation of reliable average structures. At $T^* = 0.125$, the relative difference in Gibbs free energies calculated by the two techniques reaches 0.04 NkT after ten calorimetric iterations. In contradiction with an increase in entropy due to anharmonic effects the calorimetric energy diverges from the harmonic energy in the positive direction. The shift in free energy may be attributed to an accumulation of statistical errors in the calorimetry and to poor values in free energy obtained by the determinant technique at high temperature. All the experimental distributions are fitted by Gaussian distribution. The statistical error on the Gibbs free energy is directly related to the amplitude of the statistical noise in the distributions. The deviation in Gibbs free energy at the temperature T_1^* is given by

$$\Delta G(T_1^*) = T_1^*\{\Delta G(T_0^*)/T_0^* + \Delta h_1/h_1 + \Delta h_0/h_0\} ,$$

where Δh_i corresponds to the average deviation of the noise in the distribution h_i from the Gaussian distribution. An upper limit to the standard deviation of the Gibbs free energy can be calculated with $\Delta h_i/h_i = (1/2)T^*$ when the interval of temperature is 0.005 and $\Delta h_i/h_i = T^*$ when the interval of temperature is 0.01. The maximum cumulative error on the Gibbs free energy at $T^* = 0.14$ after 12 iterations is 0.015 NkT.

We next investigated a $3d$ perfect crystal containing 108 particles. The LJ potential was truncated between the third and fourth nearest neighbors (range of interaction $R_i = 2.1\sigma$). The system was under a reduced isostatic pressure $P^* = P\sigma^3/4\epsilon\kappa = 0.1$. We conducted the simulations and the computations of free energies under the same conditions as in the $2d$ case. The energy distribution Gibbs free energies are given in Table III and Fig. 2. The calculated entropies are in reasonably good agreement with the experimental data of Kuebler and Tosi[12] in spite of the difference in pressure and the truncation of the Lennard-Jones interatomic potential in the calculations. The uncertainty on the Gibbs free energy calculated by the computer calorimetry technique does not exceed 0.02 NkT. A systematic shift from the harmonic free energy toward lower values is apparent. The relative difference reaches values as large as 0.144 NkT near the melting temperature.

The temperature dependence of the Gibbs free energy can be calculated by the traditional thermodynamic expressions if it is written as an integral over the temperature of the differential quantity

$$dG = dH - d(TS)$$

along a reversible path linking the two temperatures. Performing the integration leads to

$$G(T) = H(T) - T\left\{S(T_0) + \int_{T_0}^{T}(C_p/\theta)d\theta\right\} .$$

When the temperature interval is small, the heat capacity can be approximated by $\Delta H/\Delta T = C_p$. We have applied this approach to the calculation of the Gibbs free energy from the average enthalpy generated in the molecular dynamics simulations. The integrated free energy is in extremely good agreement with Gibbs free energy computed by computer calorimetry. They lie within 0.01 NkT of each other. The traditional approach by integration of the differential form $dG = dH - d(TS)$, however, does not make the energy distribution method at two temperatures obsolete because it is clear that one cannot apply the former to a system that un-

TABLE II. Thermodynamic data of 2D Lennard-Jones crystals calculated by molecular dynamics, the determinant technique (DET) and the computer calorimetry at two temperatures (CC). The interatomic potential was truncated between the second and third nearest neighbors. The systems were simulated under an isostatic pressure $P^* = 0.4936$. The difference in the (DET) and (CC) Gibbs free energies is given in units of NkT.

|			DET			CC			
T^*	V^*/N	H^*/N	S^*/N	F^*/N	G^*/N	S^*/N	F^*/N	G^*/N	ΔG
0.055	1.077	−0.1646	1.107	−0.7570	−0.2254	⋯	⋯		
0.060	1.080	−0.1535	1.301	−0.7646	−0.2316	1.301	−0.7646	−0.2316	0.000
0.065	1.085	−0.1410	1.497	−0.7736	−0.2383	1.501	−0.7739	−0.2385	0.003
0.070	1.087	−0.1290	1.681	−0.7835	−0.2467	1.679	−0.7833	−0.2465	0.003
0.075	1.091	−0.1183	1.827	−0.7940	−0.2553	1.827	−0.7940	−0.2553	0.000
0.080	1.095	−0.1050	2.001	−0.8057	−0.2651	2.000	−0.8056	−0.2650	0.001
0.085	1.099	−0.0936	2.143	−0.8182	−0.2757	2.138	−0.8179	−0.2754	0.003
0.095	1.109	−0.0661	2.452	−0.8463	−0.2991	2.444	−0.8456	−0.2983	0.008
0.105	1.119	−0.0373	2.743	−0.8778	−0.3253	2.733	−0.8767	−0.3243	0.009
0.115	1.129	−0.0101	3.004	−0.9127	−0.3555	2.981	−0.910	−0.353	0.022
0.125	1.138	0.0151	3.229	−0.9505	−0.3888	3.191	−0.946	−0.384	0.040
0.135	1.156	0.0577	⋯	⋯	⋯	3.522	−0.988	−0.418	⋯
0.140	1.163	0.0760	⋯	⋯	⋯	3.651	−1.009	−0.435	⋯
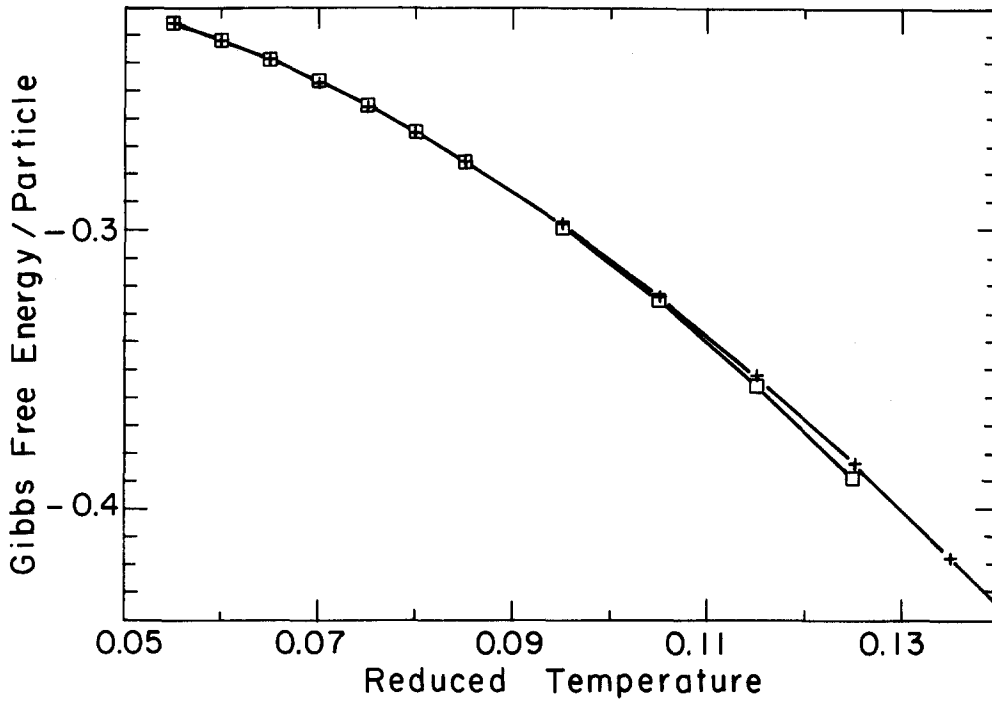
FIG. 1. Temperature dependence of the Gibbs free energy per particle of a 2D Lennard-Jones crystal containing 104 particles. The "□" and " + " were computed, respectively, with the determinant technique and computer calorimetry technique at two temperatures.

dergoes a phase transition. The energy distribution method at two temperatures can still be applied through a discontinuity in enthalpy provided that the magnitude of the discontinuity is not too big. The shift between harmonic and anharmonic free energies is then not due to an accumulation of errors in the calculations but rather represents the anharmonic contribution to the Gibbs free energy. The distributions of enthalpy of three-dimensional systems show very little noise compared to the distributions of enthalpy of two-dimensional perfect crystals. The statistical error on the Gibbs free energy one makes by applying the computer calorimetry at two temperatures to three-dimensional systems is then very much smaller than when it is applied to two-dimensional systems.

To study the effect of the range of interaction on the free energy calculation, we simulated the previous 3D crystal in the temperature interval $0.095 < T^* < 0.14$ with a slightly higher range of interaction ($R_i = 2.15\sigma$). The thermodynamic data are shown in Table IV. An increase in the range

of interaction of the interatomic potential leads to a lowering of all energies calculated as averages along trajectories. The contraction of the crystal, however, has no significant effect on the free energies obtained by the determinant technique. The data do not show a divergence between the harmonic and anharmonic Gibbs free energies. Even at high temperatures, the integrated free energies confirm the absence of anharmonic shift. The determinant technique was not applicable at $T^* = 0.1325$ and $T^* = 0.140$ because of the spontaneous formation of defects.

III. CONCLUSIONS

In this section we have applied three reliable techniques which may be routinely employed for calculating free energies using molecular dynamics. We have reported the results obtained using these techniques for calculations of the free energies of two- and three-dimensional Lennard-Jones crystals, using an isostress–isothermal formulation of molecular

TABLE III. Thermodynamic data of 3D Lennard-Jones crystals. The interaction range was taken between the third and fourth nearest neighbors ($R_i = 2.1\sigma$) and the isostatic pressure was $P^* = 0.1$. The difference in the (DET) and (CC) Gibbs free energies is expressed in units of NkT.

|			DET			CC			
T^*	V^*/N	H^*/N	S^*/N	F^*/N	G^*/N	S^*/N	F^*/N	G^*/N	ΔG
0.055	0.9782	− 1.6436	1.140	− 1.8041	− 1.7063	⋯	⋯	⋯	⋯
0.060	0.9818	− 1.6262	1.428	− 1.8101	− 1.7119	1.443	− 1.8110	− 1.7128	0.015
0.065	0.9857	− 1.6084	1.707	− 1.8180	− 1.7194	1.730	− 1.8195	− 1.7209	0.023
0.070	0.9897	− 1.5910	1.959	− 1.8271	− 1.7281	1.991	− 1.8293	− 1.7303	0.031
0.075	0.9936	− 1.5728	2.170	− 1.8349	− 1.7355	2.242	− 1.8403	− 1.7410	0.073
0.085	1.0022	− 1.5359	2.649	− 1.8614	− 1.7612	2.705	− 1.8661	− 1.7659	0.055
0.095	1.0128	− 1.4941	⋯	⋯	⋯	3.174	− 1.8969	− 1.7956	⋯
0.105	1.0228	− 1.4540	3.483	− 1.9226	− 1.8204	3.572	− 1.9314	− 1.8291	0.083
0.115	1.0345	− 1.4098	3.879	− 1.9593	− 1.8559	3.973	− 1.9701	− 1.8667	0.094
0.125	1.0485	− 1.3596	4.283	− 1.9999	− 1.8950	4.392	− 2.0135	− 1.9086	0.109
0.140	1.0733	− 1.2785	4.861	− 2.0664	− 1.9591	5.006	− 2.0866	− 1.9793	0.144
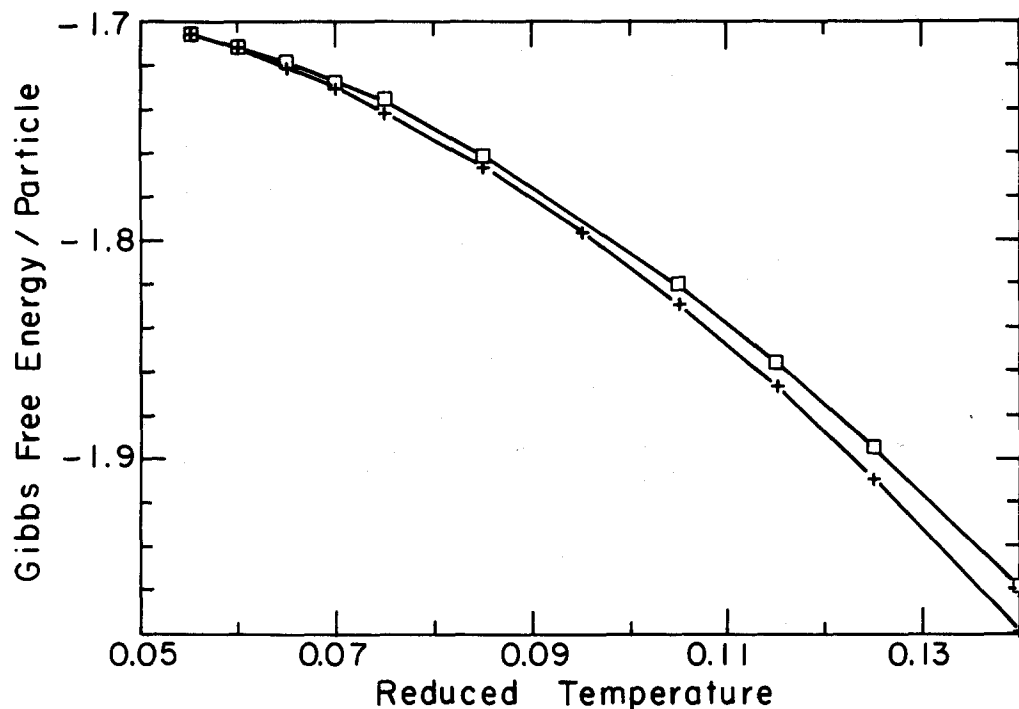
FIG. 2. Temperature dependence of the Gibbs free energy per particle of a 3D Lennard-Jones crystal containing 108 particles. The interatomic potential was truncated at $R_i = 2.1\sigma$. The □ and + were computed, respectively, with the determinant technique and computer calorimetry technique at two temperatures.

dynamics. In addition we have quantitatively characterized the efficiencies of the various techniques. It is apparent that there exist various limitations, both computational and physical, on the use of each of the techniques, which restrict the range of their applicability.

The determinant technique is very desirable because of its accuracy, if it is employed within the range of its validity; i.e., at temperatures low enough to avoid harmonic contributions to the free energy, but high enough to avoid quantum effects. In addition, with an efficient routine for calculation of the determinant of the matrix of force constant coefficients, it can be a very fast method. Other restrictions on its use exist, however, which can be very cumbersome. First of all, it is based on the generation of an average structure, from which the matrix of force constant coefficients may be computed. When molecular dynamics simulations are conducted at high temperatures, and particularly when crystalline defects are present, the spontaneous generation of defects, and the high mobility of any defects which may be present, may render any average structure physically meaningless, and useless for the determinant technique. Related to this difficulty is the fact that the determinant technique only ac-

cesses the vibrational contribution to the entropy; no contribution to configurational entropy can be examined. Additional complications arise in the implementation of the determinant technique. There will be severe computational restrictions on the size of the matrices for which the determinant can be computed. This computational restriction can be lifted by simulating systems under fixed or free border conditions instead of periodic boundary conditions. When fixed or free boundary conditions are applied the matrix of the force constant coefficients is "banded" and very powerful algorithms to compute the determinant of banded matrices exist. In addition, in the process of going from the determinant to the free energy value, we have to handle numbers of great magnitude, which places severe restrictions on the number of particles in the system. When using the quasiharmonic approximation for defects, the question about whether the atoms in the defect can be considered to behave harmonically arises. This question has, however, not been answered and one has to make the assumption that the quasiharmonic approximation may be used for atoms in or near a defect, at least for the low temperature range.

An additional problem arises when fitting the calculated

TABLE IV. Thermodynamic data of 3D Lennard-Jones crystals. The interaction range was taken between the third and fourth nearest neighbors ($R_i = 2.15\sigma$). The isostatic pressure is $P^* = 0.1$. The difference in the (DET) and (CC) Gibbs free energies is expressed in units of NkT.

			DET			CC			
T^*	V^*/N	H^*/N	S^*/N	F^*/N	G^*/N	S^*/N	F^*/N	G^*/N	ΔG
0.095	1.0115	-1.5024	3.005	-1.8891	-1.7873	$\cdots$	$\cdots$	$\cdots$	$\cdots$
0.110	1.0253	-1.4458	3.560	-1.9400	-1.8375	3.560	-1.9400	-1.8375	0.000
0.120	1.0368	-1.4034	3.925	-1.9781	-1.8744	3.930	-1.9788	-1.8751	0.006
0.130	1.0490	-1.3591	4.287	-2.0213	-1.9164	4.285	-2.0211	-1.9162	0.001
0.1325	1.05195	-1.3480	$\cdots$	$\cdots$	$\cdots$	4.370	-2.0323	-1.9220	$\cdots$
0.140	1.0646	-1.3083	$\cdots$	$\cdots$	$\cdots$	4.667	-2.0681	-1.9616	$\cdots$

distributions. If we want accurate values for the free energy differences, we need to have smooth, well-characterized distributions. In the case of the computer calorimetry technique at two temperatures the distribution can be fitted with good agreement by a Gaussian distribution. On the other hand, in the case of the computer calorimetry technique for systems having different Hamiltonians, no simple mathematical argument is available to fit the experimental distributions. One has to turn to empirical fitting, with its associated pitfalls. In addition there can be the problem of insufficient overlap of the distributions. Invoking intermediate Hamiltonians or temperatures can always, in principle, be done, but only with a concommitant increase in systematic error accumulation. The interpolation technique can be used but will introduce the intrinsic errors of interpolation. An additional restriction to the computer calorimetry techniques is that the two systems of interest must be defined on the same configuration space. This complicates the study, for example, of free energy differences between arbitrary polymorphic phases. While this limitation can be overcome if the path in configuration space between the two phases is prescribed,[13] it certainly represents an additional level of computational complexity. Lastly, the computer calorimetry techniques have the major limitation that they only provide estimates of free energy differences, and not absolute values of the free energies of the systems of interest. Of course, for some problems, the free energy difference is the quantity of interest. For other problems, however, when an absolute value is required, one has to use a reference system of known free energy, which, in itself imposes major restrictions on the technique.

In summary, the techniques described allow one to access, with a satisfactory accuracy, the free energies of many systems of interest. The nature of the particular problem will dictate which of the techniques should be employed, and the details of their most efficient implementation. Because knowledge of free energies is crucial to the understanding of such a huge number of important phenomena, it will often be worthwhile to employ one or more of the methods, in spite of the limitations that are inherent to them.

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