

Temperature Dependence of Thermodynamic Quantities from Simulations at a Single Temperature

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A new method is developed for obtaining thermodynamic information over a wide range in parameter space from a series expansion involving the first few cumulants of a distribution function which is generated at one point in parameter space. The method is employed to obtain the temperature dependence of the Gibbs free energy, the enthalpy, and the lattice parameter of a Lennard-Jones crystal from Monte Carlo simulations. Good agreement with independent calculations is found over a temperature range of approximately 75% of the melting temperature.

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The Monte Carlo (MC) method has been used extensively to perform controlled computer simulations in which the ensemble averages of various thermodynamic quantities are calculated. In many cases, the object of these studies is to determine the dependence of averaged quantities, such as the free energy or the lattice parameter of a solid, on some variable thermodynamic parameter, such as the temperature or pressure. While this is usually accomplished by performing a series of simulations at different values of the thermodynamic parameter, it is possible, in principle, to determine the dependence of these averaged quantities on a given parameter by doing simulations at only *one* point in parameter space.¹⁻³

For example, MacDonald and Singer¹ used a histogram method in order to calculate some thermodynamic properties of liquid argon. In this method a histogram of the potential energies corresponding to many distinct configurations generated in a MC simulation at a fixed temperature T_1 was constructed. By suitably reweighting the original histogram, histograms corresponding to different temperatures T were obtained and then used to calculate such quantities as the pressure and the heat capacity. However, because the high- and low-energy wings of the original histogram, which are sampled comparatively rarely, contribute significantly to the reweighted histograms, particularly for $|T - T_1|$ large, the range of temperatures that could be probed by this method was limited to about $(1 \pm 0.15)T_1$.

More recently, Alves, Berg, and Villanova⁴ and Ferrenberg and Swendsen⁵ have used the histogram method to calculate the density of states for the three-dimensional Ising model and critical temperature and the specific heat at the critical temperature of the eight-state Potts model, respectively. While this method is ideally suited for the accurate determination of thermodynamic information near phase transitions, the range of parameter space that can be explored is limited by the size of the system under study.⁶ Further, rather long simulations consisting of up to 8×10^6 Monte Carlo steps (MCS) are needed in order to accurately determine the

histogram. Such long simulations are impractical for the study of the thermodynamics of liquids and solids that are described by continuous potentials.

In this Letter we present a new, computationally efficient method for calculating various thermodynamic functions over a wider range in parameter space within a single-phase region than is generally possible with the histogram method. The central advance of the new method is to systematically analyze the distribution function obtained at a fixed parameter in terms of its cumulants. Such an analysis provides three benefits. First, it shows that only the lowest-order cumulants of the distribution function, which are well determined by simulation, are necessary for the accurate calculation of many thermodynamic quantities. Second, by effectively smoothing the histogram obtained in the simulation, it provides a controlled, analytic approximation to the distribution function, the wings of which are poorly determined from simulation.⁷ Third, it largely obviates long MC simulations and is not restricted to small system sizes. This new method can be viewed as being complementary to the histogram method in that it is well suited to the study of thermodynamic properties over a wide range of parameters away from phase transitions. We validate the method by calculating the temperature dependence of the Gibbs free energy G per particle, the enthalpy H per particle, and the lattice parameter a of a perfect fcc crystal from an analysis of the enthalpy distribution function in terms of its cumulants as obtained from isobaric MC simulations at one fixed temperature T_1 .

Consider a solid consisting of N particles of equal mass which is confined to a cell of volume V at some (inverse) temperature $\beta = 1/k_B T$, where k_B is Boltzmann's constant. The particles interact via a potential $U(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3, \dots, \mathbf{R}_N)$, where \mathbf{R}_n is the location of particle n in configuration space. The isobaric configurational partition function $Z(\beta, p, N)$ is given by

$$Z(\beta, p, N) = C \int_0^\infty dV Z(\beta, V, N) \exp\{-\beta p V\}, \quad (1)$$

where

$$Z(\beta, V, N) = \int_V d^{3N} \mathbf{R} \exp\{-\beta U(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3, \dots, \mathbf{R}_N)\},$$

C is a normalization constant, and p is the pressure. The configurational canonical average $\langle A \rangle_{\beta, p, N}$ of some quantity A , such as H or a , can be obtained by performing a simulation at fixed β_1 , N , and p and evaluating

$$\Delta A \equiv \langle A \rangle_{\beta, p, N} - \langle A \rangle_{\beta_1, p, N} = \frac{\langle \delta A \exp[-(\beta - \beta_1)H] \rangle_{\beta_1, p, N}}{\langle \exp[-(\beta - \beta_1)H] \rangle_{\beta_1, p, N}}, \quad (2)$$

where $\delta A = A - \langle A \rangle_{\beta_1, p, N}$ and the ensemble averages $\langle \rangle$ are to be performed at constant β_1 , p , and N hereafter. Equation (2) is, then, a prescription for calculating ΔA

$$\chi(r, \lambda) = \frac{\partial^r}{\partial \lambda'^r} \left[\sum_n \sum_m' (-1)^n \frac{(\beta - \beta_1)^n}{n!} \frac{\lambda'^m}{m!} \langle H^n (\delta A)^m \rangle_C \right] \Big|_{\lambda' = \lambda}, \quad (4)$$

where the prime in the summation means that the term with $n = m = 0$ is omitted and where $\langle \rangle_C$ denotes a cumulant calculated at β_1, p, N . In particular, for $r = \lambda = 0$,

$$\Delta(\beta G) = \sum_{n=1}^{\infty} \frac{(\beta - \beta_1)^n}{n!} (-1)^{n+1} \langle H^n \rangle_C, \quad (5)$$

and for $r = 1$ and $\lambda = 0$

$$\Delta A = \sum_{n=1}^{\infty} \frac{(\beta - \beta_1)^n}{n!} \left[\frac{\partial^n (\Delta A)}{\partial \beta^n} \right]_{\beta = \beta_1} = \sum_{n=1}^{\infty} \frac{(\beta - \beta_1)^n}{n!} (-1)^n \langle (\delta A) (\delta H)^n \rangle_C. \quad (6)$$

These results can be viewed as linked-cluster expansions⁹ for the quantities $\Delta(\beta G)$ and ΔA .

over a range in temperature from a simulation which is performed at a single temperature T_1 .

It is convenient at this point to introduce a joint moment-generating function

$$\Phi(\lambda) = \langle \exp[-(\beta - \beta_1)H + \lambda \delta A] \rangle, \quad (3)$$

where λ is a "field." We then define $\chi(r, \lambda) = \partial^r \ln \Phi(\lambda') / \partial \lambda'^r |_{\lambda' = \lambda}$, where λ' is set equal to λ after performing the differentiation, as indicated. $\chi(r, \lambda)$ is a two-parameter generating function. It can be shown that

$$\chi(0, 0) = -\Delta(\beta G) = \beta_1 G(\beta_1, p, N) - \beta G(\beta, p, N)$$

and $\chi(1, 0) = \Delta A$. Using the definition of the generalized cumulant expansion,⁸ the moment-generating function $\Phi(\lambda)$ can be expanded in cumulants, and then

The representation of $\Delta(\beta G)$ over a wide temperature range by a series expansion in powers of $\beta - \beta_1$ [Eq. (5)] is natural since, from thermodynamics, G remains finite and so $\Delta(\beta G)$ diverges as $T \rightarrow 0$ for a nonzero simulation temperature T_1 . By contrast, it is more natural to expand quantities that remain finite as $T \rightarrow 0$, such as H or a , in powers of $T - T_1$. Now, by rewriting Eq. (6) in terms of the temperature T and then expanding $(1/T)^n$ in a Taylor series about a simulation temperature T_1 , ΔA can be expanded in a Taylor series about T_1 by

$$\Delta A = \sum_{l=1}^{\infty} \frac{1}{l!} \left[\frac{\partial^l (\Delta A)}{\partial T^l} \right]_{T=T_1} (T - T_1)^l, \quad (7)$$

where

$$\left[\frac{\partial^l (\Delta A)}{\partial T^l} \right]_{T=T_1} = \left[\frac{1}{T_1} \right]^l \sum_{n=1}^l \frac{(-1)^{l-n}}{n!} \binom{l-1}{l-n} \langle \delta A [\delta(\beta_1 H)]^n \rangle_C. \quad (8)$$

Equations (5) and (7) will be the starting points for the determination of $\Delta(\beta G)$ and ΔA , explicitly, over a range in temperature from information gathered at a single temperature. In order to calculate them explicitly, it is necessary to truncate the infinite-series expansions, thereby retaining only the few, lowest-order cumulants. While this truncation, in principle, restricts the range of parameter space that can be explored with this method, in practice one can still explore a rather wide range of parameter space with the limited amount of information contained in the lower-order cumulants.

The system that we have simulated is a defect-free fcc crystal consisting of $N = 108$ particles that interact via a Lennard-Jones potential with energy and length parameters ϵ and σ , respectively, that was smoothly shifted to zero and cut off between the fourth- and fifth-neighbor shells. Periodic boundary conditions were employed to eliminate edge effects. The reference temperature T_1 used in the simulation for the calculation of the cumulants was $0.206\epsilon/k_B$ (400 K for bulk copper) with corresponding lattice parameter $a = 1.012a_0$, where the zero-temperature lattice parameter $a_0 = 1.562\sigma$. This choice of reference temperature was made for convenience and simulations performed at a different reference temperature, $0.309\epsilon/k_B$, gave equally satisfactory results.

As a first test of the utility of this method, we have calculated $\Delta(\beta G)$ for the crystalline solid by using Eq. (5) and the first three enthalpy cumulants $\langle (\delta H)^n \rangle_C$ ($n = 1, 2, 3$) of the enthalpy distribution function calculated in the simulations. From thermodynamics, $\Delta(\beta G)$ can also be calculated at constant pressure from the relation $\Delta(\beta G) = \int_{\beta_1}^{\beta} H(\beta') \times d\beta'$, where $H(\beta)$ is calculated in a series of simulations at different β . In order to calculate the Gibbs free energy G as a function of temperature, it is necessary to independently determine G at some reference temperature. For solids,

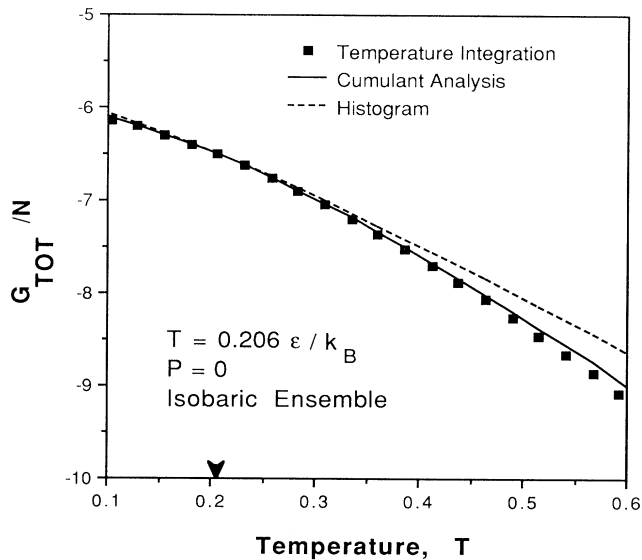


FIG. 1. The total Gibbs free energy G_{TOT}/N , in units of ϵ , vs temperature T , in units of ϵ/k_B , for a defect-free Lennard-Jones crystal consisting of 108 particles. The solid squares are the results of temperature integration, the solid line is the result of a cumulant expansion at a fixed simulation temperature $T=0.206\epsilon/k_B$ (indicated by the arrow), and the dashed line is the result of a histogram evaluation.

this can be done at low temperatures by using the quasiharmonic approximation.^{10,11}

Figure 1 shows the total Gibbs free energy per particle G_{TOT}/N (which includes the ideal-gas contribution) calculated (a) by means of the truncated cumulant expansion, (b) from the (inverse) temperature-integration method, and (c) from an enthalpy histogram compiled in the simulations at temperature T_1 . Approximately 1×10^5 MCS were used in the calculation of the cumulants while about 6.3×10^5 MCS were used in order to compile the associated histogram. As is evident from the figure, the results obtained from the histogram method match those obtained from the temperature-integration method only over a rather limited range in temperature. By contrast, the truncated cumulant expansion and the temperature-integration method yield nearly identical results over a wide range in temperature (about $0.45\epsilon/k_B$, which is approximately 75% of the melting temperature), indicating that the representation of $\Delta(\beta G)$ by only a few terms in the cumulant expansion is satisfactory. An analysis of simulations consisting of approximately 10^5 MCS for systems containing $N=108$ to $N=512$ particles reveals that the cumulants obey the expected finite-size scaling relation, $\langle H^n \rangle_C \propto N$. Thus, even for relatively large system sizes, the free energy can be calculated over an equally wide range in temperature.¹¹

The correct determination of G_{TOT}/N from the truncated cumulant expansion suggests, then, that the depen-

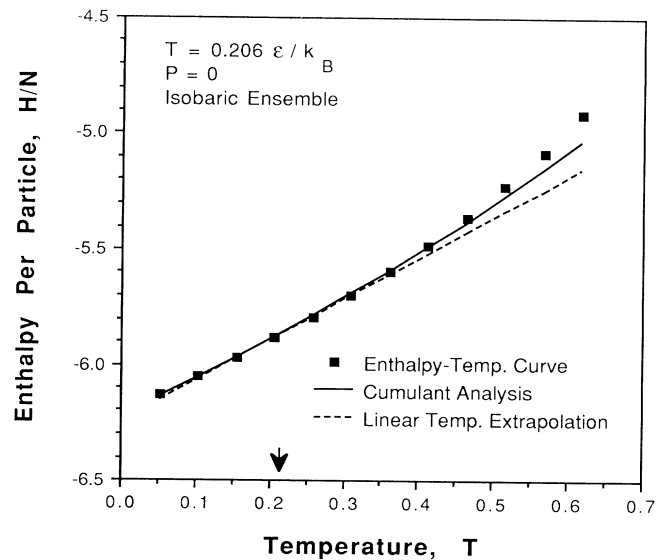


FIG. 2. The configurational enthalpy per particle, H/N , vs temperature T as obtained from the enthalpy-temperature curve generated from several simulations at different temperatures, from a linear extrapolation based on only the first cumulant, and from a cumulant analysis [Eq. (8)].

dence of other thermodynamic functions, such as the enthalpy and the lattice parameter of the crystal, on temperature should also be obtainable from an analysis of a distribution function. Figures 2 and 3 are plots of

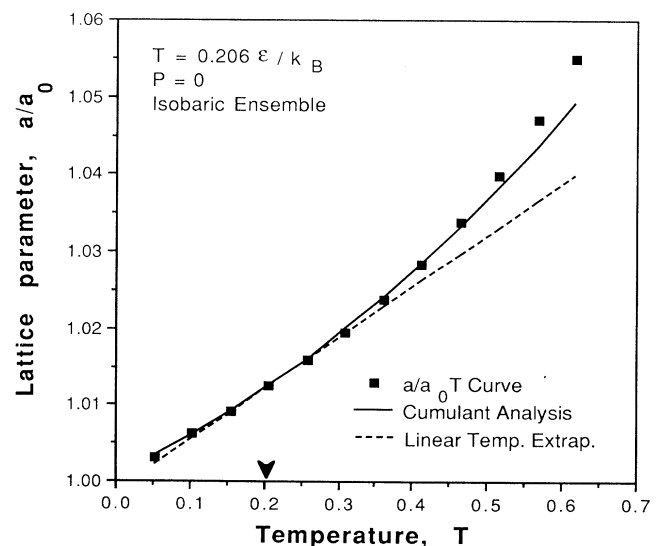


FIG. 3. The normalized lattice parameter a/a_0 (where a_0 is the zero-temperature lattice parameter) vs T as obtained from the a/a_0 - T curve generated from several simulations at different temperatures, from a linear extrapolation based on only the first cumulant, and from a cumulant analysis.

H/N and a/a_0 as a function of temperature as obtained from Eq. (8) with $\langle(\delta H)^n\rangle_C$ ($n=1,2,3$) and $\langle\delta a(\delta H)^n\rangle_C$ ($n=1,2$) and from a series of simulations at different temperatures. The two independent determinations of H/N and a/a_0 agree over a wide temperature range. It was found that somewhat longer simulations (in this case, approximately 7×10^5 MCS) were required in order to accurately calculate $\langle(\delta H)^3\rangle_C$ and $\langle\delta a(\delta H)^2\rangle_C$ and, consequently, $H(T)$ and $a(T)$.

In conclusion, we have demonstrated that thermodynamic functions can be efficiently calculated at various points in parameter space (in this case temperature) from a simulation at one point in parameter space and, in so doing, have identified those features of the distribution function, namely, the cumulants, which are relevant in these calculations. The application of this method, is of course, not limited to the isobaric, canonical ensemble nor to homogeneous crystals, but is generally applicable to the cases of, for example, fluids and inhomogeneous solids (such as those with extended imperfections).¹¹ The dependence of other quantities, such as elastic constants, on other intensive parameters, such as the pressure and the chemical potential, can also be obtained by a simple generalization of this method.

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