Calculation of microcanonical entropy differences from configurational averages

Sergio Davis[*]

Grupo de Nanomateriales, Departamento de Física, Facultad de Ciencias, Universidad de Chile, Casilla 653, Santiago, Chile

A simple expression is derived, enabling the calculation of the entropy difference between two microcanonical equilibrium states at different energies in atomistic computer simulations. This expression only requires potential energy samples from molecular dynamics or Monte Carlo simulations at the relevant energies. This presents an alternative to switching methods such as thermodynamic integration or nonequilibrium work relations, as well as flat-histogram random walks, all of which involve sampling *in between* the relevant states. The method is especially suited for small (nanoscopic) systems such as clusters and proteins, and is applicable to first-principles data directly.

Entropy is a fundamental quantity in thermodynamics, having great importance in physics and chemistry, not to mention it being recognized as one of the most enigmatic concepts in nature [1]. It is connected with the lack of information about the microscopic state when fixing a given set of macroscopic variables, and to the second law of thermodynamics, which describes the notion of *irreversibility* and the *arrow of time* [2].

The microcanonical ensemble, describing an isolated system with a fixed number of particles N, fixed energy E, and fixed volume V, has recently regained interest over the traditional canonical ensemble (where the temperature T is considered fixed instead of the energy), mainly in the context of small systems (far from the thermodynamic limit) [3–7] but also for long-ranged interactions where ensemble equivalence does not hold, even in the thermodynamical limit [8].

In microcanonical thermodynamics, knowledge of the entropy $S = S(N,V,E)$ is the fundamental relation that fully describes the system [9]. From a more practical point of view, entropy differences are relevant in first-order phase transitions and seem to be deeply connected to protein folding energetics [10–12]. Direct calculation of the microcanonical entropy in atomistic simulations, however, involves an intrinsic computational challenge: namely, the estimation of the phase-space volume in which the system evolves, which is related to the problem of counting the number of states for discrete systems. Thus, other approaches have been preferred instead, such as thermodynamic integration [13], and nonequilibrium work relations, such as the Jarzynski equality [14], for the determination of free-energy differences, and indirectly obtaining the entropy difference from them. Recently, Adib [15] has derived the microcanonical equivalent of the Jarzynski equality, which can be used to calculate isoenergetic entropy differences using a switching parameter. Another widely used technique for the determination of entropy is the Wang-Landau (WL) algorithm [16,17], originally developed for discrete models but soon generalized to the continuous case [18]. WL techniques consist of performing a random walk in energy space with the goal of achieving a flat histogram of energies. The density of states is updated in the process, and finally converges to its true value.

In this Rapid Communication, a method for direct computation of the microcanonical entropy difference between two energies (possibly different phases of the same system) is presented. This method only involves averages at the initial and final states, without any need to invoke switching between those states or flat-histogram random walks.

Microcanonical averages. We will consider a classical system of $6N$ degrees of freedom ($3N$ momenta, denoted collectively by $\mathbf{p}$, $3N$ coordinates denoted by $\mathbf{r}$), with the Hamiltonian

$$\mathcal{H} = \frac{\mathbf{p}^2}{2m} + \Phi(\mathbf{r}). \qquad (1)$$

The probability of the system having phase-space coordinates $(\mathbf{r},\mathbf{p})$ at a fixed total energy E is given by [19,20]

$$P(\mathbf{r},\mathbf{p};E) = \frac{1}{\Omega(E)}\delta(E - \mathcal{H}(\mathbf{r},\mathbf{p})), \qquad (2)$$

where

$$\Omega(E) = \frac{1}{h^{3N}} \int d\mathbf{r}\,d\mathbf{p}\,\delta(E - \mathcal{H}(\mathbf{r},\mathbf{p})) \qquad (3)$$

is the density of states having energy between E and $E + dE$, and h is Planck's constant. From this density of states, the microcanonical entropy is obtained by using Boltzmann's formula

$$S(E) = k_B \ln \Omega(E).$$

Given that the dependence of the Hamiltonian on $\mathbf{p}$ is fully known, those degrees of freedom can be removed from the problem by integrating them explicitly [21,22]. To do this, we separate $\mathcal{H}$ inside the delta function and use

$$\int d\mathbf{p}\,\delta(E - \mathbf{p}^2/2m - \Phi(\mathbf{r})) \rightarrow \int_{\Sigma_p} \frac{d\Sigma_p}{|\nabla(\mathbf{p}^2/2m)|}, \qquad (4)$$

where the last integral is over the surface Σ_p of an hypersphere of dimension $3N$ and radius

$$|\mathbf{p}| = \sqrt{2m(E - \Phi(\mathbf{r}))}.$$

Upon replacing the area of the hypersphere [23], we can rewrite Eq. (2) as

$$P(\mathbf{r};E) = \frac{1}{\eta(E)}\Theta(E - \Phi(\mathbf{r}))\sqrt{E - \Phi(\mathbf{r})}^{\,3N-2}, \qquad (5)$$

where $\eta(E)$ is defined as

$$\eta(E) = \int d\mathbf{r}\, \Theta(E - \Phi(\mathbf{r}))\sqrt{E - \Phi(\mathbf{r})}^{3N-2} \qquad (6)$$

and $\Theta(x)$ is Heaviside's step function, defined under the convention

$$\Theta(x) = \begin{cases} 0, & x \leqslant 0, \\ 1, & x > 0. \end{cases}$$

Note that a constant factor

$$\alpha = \frac{3N}{2h^{3N}} \frac{\sqrt{2\pi m}^{3N}}{\Gamma(1 + 3N/2)},$$

coming from the area of Σ_p, cancels out when deriving Eqs. (5) and (6), and therefore $\Omega(E)$ is proportional to $\eta(E)$ with a proportionality factor independent of E. We will refer to either Ω or η as the density of states: For the purposes of computing the microcanonical entropy they are completely equivalent, because $S(E) = k_B \ln \eta(E) + S_0$, with S_0 a constant shift.

Using Eq. (5) we can define the microcanonical expectation value of any configurational quantity $A(\mathbf{r})$ as

$$\langle A \rangle_E = \frac{1}{\eta(E)} \int d\mathbf{r}\, \Theta(E - \Phi(\mathbf{r}))\sqrt{E - \Phi(\mathbf{r})}^{3N-2} A(\mathbf{r}). \quad (7)$$

Entropy differences. We can devise a configurational quantity $\sigma(\mathbf{r})$ such that $\langle \sigma \rangle_E$ depends on E only through $\Omega(E)$, i.e., where the integral in Eq. (7) is independent of E. Then knowledge of $\langle \sigma \rangle$ at two different energies E and E' should give us the entropy difference

$$\Delta S = S(E') - S(E) = k_B \ln \frac{\Omega(E')}{\Omega(E)}$$

without information about the intermediate states. For the use of this method in computer simulations, a second requirement for the choice of σ is that it should be easily computable. We proceed to show that the choice

$$\sigma(\mathbf{r}; E_0) = \frac{\Theta(E_0 - \Phi(\mathbf{r}))}{\sqrt{E - \Phi(\mathbf{r})}^{3N-2}} \qquad (8)$$

for $E_0 < E$ fulfills this purpose. Substituting Eq. (8) into Eq. (7), we get

$$\langle \sigma \rangle_{E, E_0} = \frac{1}{\eta(E)} \int d\mathbf{r}\, \Theta(E_0 - \Phi(\mathbf{r})) = \frac{d(E_0)}{\eta(E)}, \qquad (9)$$

in which it can be clearly seen that the integral $d(E_0)$ does not depend on the value of E, only on the value of the reference energy E_0 and the potential energy function Φ. In fact, this integral represents the volume in configurational space enclosed by the surface $\Phi(\mathbf{r}) = E_0$, and this is a geometric property independent of any ensemble or energy.

From this choice of σ it follows that the entropy difference ΔS can be obtained as

$$\Delta S = k_B \ln \frac{\langle \sigma \rangle_{E, E_0}}{\langle \sigma \rangle_{E', E_0}}, \qquad (10)$$

from which it seems convenient to write

$$S(E) = -k_B \ln \langle \sigma \rangle_{E, E_0} + S_0. \qquad (11)$$

Use in molecular dynamics or Monte Carlo simulations. Equations (8) and (10) constitute the main result of this Rapid

Communication, and provide an alternate method, hereafter referred to as the σ method. Suppose we want to calculate ΔS between two energy states E and E', where we assume $E' > E$ with no loss of generality. We perform separate microcanonical simulations of the system at E and E', recording n_ϵ potential energy samples $\phi_i^{(\epsilon)}$, with $i = 1, \ldots, n_\epsilon$ and $\epsilon = E, E'$. We then choose a reference energy E_0 such that $E_0 < E$ (a detailed criterion for this choice is proposed below) and compute

$$\langle \sigma \rangle_{E, E_0} = \frac{1}{n_E} \sum_{\phi_i < E_0} \frac{1}{\sqrt{E - \phi_i^{(E)}}^{3N-2}}, \qquad (12)$$

$$\langle \sigma \rangle_{E', E_0} = \frac{1}{n_{E'}} \sum_{\phi_i < E_0} \frac{1}{\sqrt{E' - \phi_i^{(E')}}^{3N-2}}, \qquad (13)$$

where the summation is performed *only on the samples with* $\phi < E_0$. From this, ΔS is given directly by Eq. (10). The σ method is applicable to any microcanonical simulation technique capable of producing potential energy samples—this includes both classical and *ab initio* molecular dynamics, as well as microcanonical Monte Carlo methods [24,25].

Entropy for a Lennard-Jones system. Figure 1 shows the microcanonical entropy as a function of energy for a highly densified fcc Lennard-Jones crystal (using argon parameters $\sigma = 3.41$ Å and $\epsilon/k_B = 119.8$ K) composed of $3 \times 3 \times 3$ unit cells (108 atoms), and a lattice constant $a = 4.2$ Å. Circles in the figure represent the calculation using the σ method. The solid line represents the result of numerical integration of the inverse temperature

$$\Delta S = \int_{E \to E'} dS = k_B \int_E^{E'} d\epsilon\, \beta(\epsilon), \qquad (14)$$

using the fact that $T\, dS = dE$. Integration was implemented using a cubic spline interpolation on $\beta(E) = 1/k_B T(E)$ between discrete points.
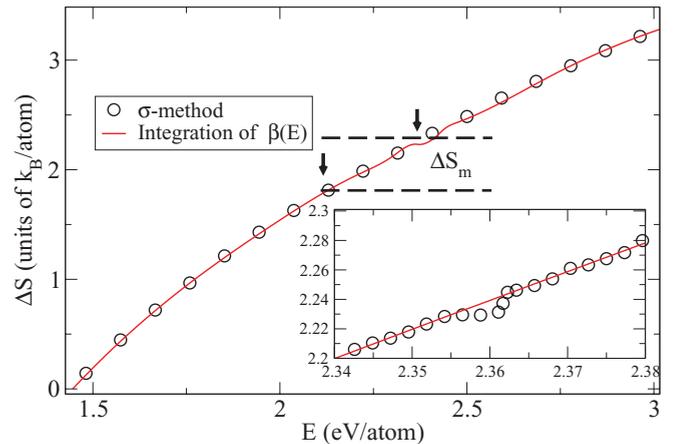

FIG. 1. (Color online) Entropy difference ΔS vs internal energy E for a highly densified 108-atom Lennard-Jones system. Circles were calculated using the σ method presented in this work, and the solid line using integration of the inverse temperature. From left to right, the arrows indicate the energies required to obtain solid and liquid at the melting temperature T_m, and the dashed lines indicate the entropies measured with the σ method at those energies.
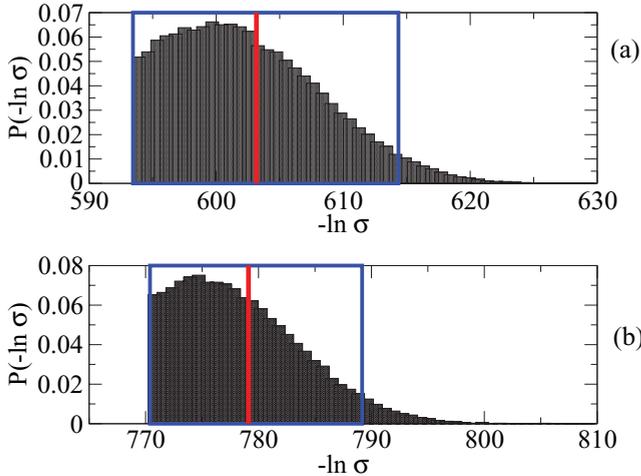
FIG. 2. (Color online) Probability density functions for $-\ln\sigma(\mathbf{r};E_0)$ at (a) $E = 150$ eV, $E_0 = 110$ eV and (b) $E = 330$ eV, $E_0 = 210$ eV. In each case, the solid blue rectangle indicates the 95% confidence interval, while the solid red line indicates the expectation value $-\langle\ln\sigma\rangle$.

The σ method closely follows the curve obtained from integration, and the inset shows a closeup of the energy region where a first-order phase transition (melting of the fcc crystal, at $T_m = 5980$ K) is observed. As the values of $\gamma = -\ln\sigma(\mathbf{r};E_0)$ are distributed according to what looks like a truncated Gaussian distribution (see Fig. 2), an estimation of its variance is not enough to appropriately construct a confidence interval (for instance, at 95% confidence) and therefore estimate the statistical error in the entropy measurements. We can obtain such an interval by integrating the probability distribution function shown in Fig. 2 from its minimum value $\gamma_{\min}$ up to an upper limit $\gamma_{\max}$ such that the cumulative distribution function reaches 0.95. We see that the average $\langle\gamma\rangle_{E,E_0}$, which is slightly larger ($\sim$1% in the energy interval considered in Fig. 1) than $-\ln\langle\sigma\rangle$ by virtue of the Jensen inequality

$$\ln\langle f\rangle \geqslant \langle\ln f\rangle,$$

always falls inside this range. For all points computed with the σ method in Fig. 1 the statistical error in $S(E)$ following the procedure outlined above was estimated to be below 2%, and accordingly, the statistical error in the differences ΔE (being additive) can be estimated to be below 4%, equal to or smaller than the size of the symbols in Fig. 1.

The integration method reveals a small dip (change in concavity) as reported in previous simulations and experiments on microcanonical phase transitions [26,27], while the σ method predicts, besides the same change in concavity, a small jump in entropy. The entropy of melting $\Delta S(T_m) = S_{\text{liquid}}(T_m) - S_{\text{solid}}(T_m)$ was determined from simulations at T_m in the solid and liquid phases, yielding a value $\Delta S(T_m) = 0.487k_B/\text{atom}$ (see Fig. 1, dashed lines) which is lower than the high-pressure limit, namely, $\Delta S(T_m) = k_B\ln 2$ [28]. This value is in quite good agreement with the one obtained from the latent heat of melting $L_m = 0.2452$ eV/atom, measured in the same simulations as the difference in potential energies at
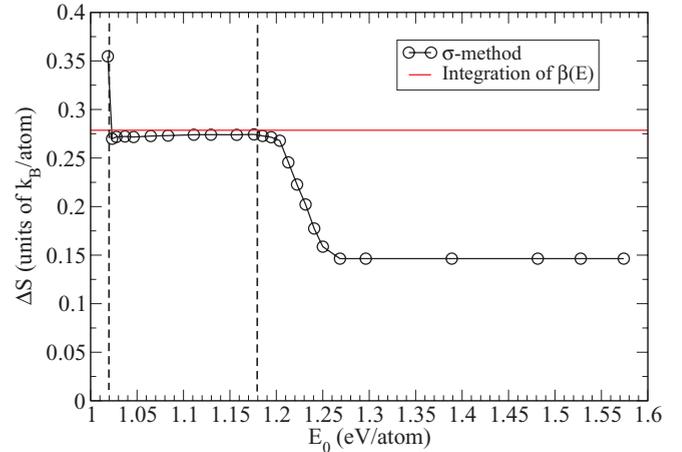

FIG. 3. (Color online) Estimated entropy difference ΔS between $E = 170$ eV and $E' = 180$ eV, as a function of the reference energy E_0 employed.

T_m. From this, the entropy of melting is $\Delta S(T_m) = L_m/T_m = 0.483k_B$.

Efficiency considerations. Equation (8) leaves room for choosing the reference energy E_0 arbitrarily, as long as $E_0 \leqslant \min(E,E')$. In practice, however, the choice of E_0 may affect the efficiency of the averages, as shown explicitly in Fig. 3. Here the entropy difference between $E = 170$ eV and $E' = 180$ eV is plotted against the reference energy E_0, using the result from integration [Eq. (14)] as a control. Choosing E_0 between 1.02 and 1.18 eV/atom seems to yield optimal results: Outside this range, either one of the probability density functions $P_E(\Phi)$ or $P_{E'}(\Phi)$ becomes so small that those states are not sampled correctly in the simulation.

In fact, the results of Fig. 4 suggest that the optimality criterion for E_0 should be the following: E_0 should maximize the joint probability $P_E(\Phi = E_0) \times P_{E'}(\Phi = E_0)$. Then, approximating $P_E(\Phi)$ as a Gaussian distribution with mean μ_E and variance σ_E, the optimal E_0 is given
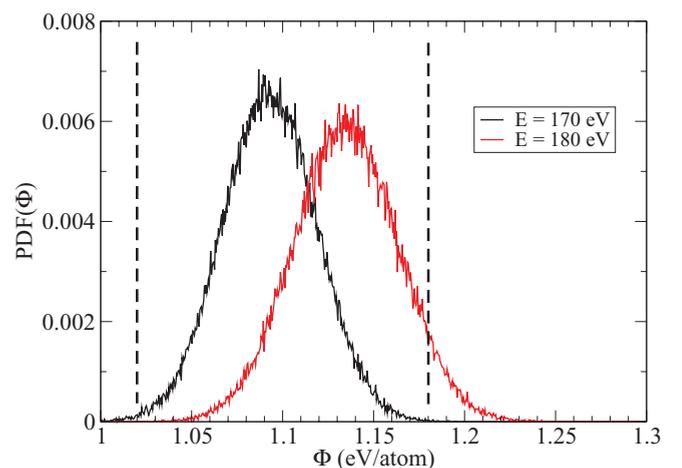

FIG. 4. (Color online) Probability density functions (PDFs) for the potential energy Φ at $E = 170$ eV and $E' = 180$ eV. Vertical dashed lines represent the lower (1.02 eV/atom) and upper (1.18 eV/atom) limits for optimal averages in Fig. 3.

by

$$E_0 = \alpha \mu_{E'} + (1 - \alpha)\mu_E, \qquad (15)$$

where

$$\alpha = \frac{\sigma_E^2}{\sigma_{E'}^2 + \sigma_E^2}.$$

In the current case, this yields $E_0 \approx 1.12$ eV/atom [at the intersection of the probability density functions (PDFs) in Fig. 4].

The need for a certain amount of overlapping between the PDFs limits the application of the method to systems such that potential energy fluctuations are of the order of (or larger than) the energy difference between the states. In order to quantify this limitation more precisely, we may impose that the probability of Φ being less than E_0 must not fall below a certain threshold p_t for either E or E', otherwise $\sigma(\mathbf{r}; E_0)$ could be poorly sampled. Under the Gaussian approximation for $P_E(\Phi)$, this condition leads to

$$\text{erf}\left[\frac{-\sigma_E \Delta \mu}{\sqrt{2}(\sigma_E^2 + \sigma_{E'}^2)}\right] \geqslant 2p_t - 1, \qquad (16)$$

$$\text{erf}\left[\frac{-\sigma_{E'} \Delta \mu}{\sqrt{2}(\sigma_E^2 + \sigma_{E'}^2)}\right] \geqslant 2p_t - 1, \qquad (17)$$

where

$$\text{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x dt \, e^{-t^2}$$

is the error function, and $\Delta \mu = \mu_{E'} - \mu_E$ is the difference of average potential energies. In a microcanonical system, σ_E is also the variance of the kinetic energy, related to the number of degrees of freedom N and the specific heat per atom c_v through Lebowitz's formula [29]

$$\sigma_E^2 = \frac{3N}{2\beta^2}\left(1 - \frac{3k_B}{2c_V}\right).$$

This relates the range of applicability of the method, in terms of the admissible energy difference $\Delta E = E' - E$, to the number of degrees of freedom N: For small systems, ΔE can be chosen to be larger. This is not as strong a limitation as it first seems, because in systems with few degrees of freedom, such as metallic clusters, proteins, and other nanoscopic systems, the fluctuations can be large enough. The main field of application envisioned here is first-principles molecular dynamics simulations, where small systems are mandatory and switching methods or WL random walks are impractical.

Concluding remarks. In summary, a method for the direct computation of microcanonical entropy differences is presented, based on sampling the configurational volume enclosed by a reference value of potential energy E_0 as seen from two different energy states. The method is envisioned for small systems where potential energy fluctuations are large enough to cross the total energy gap between states with some nonvanishing probability. It has shown to be precise enough to reproduce the convex dip observed at the transition energies in small Lennard-Jones systems.

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