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Abstract. In this work we develop a method for inferring the underlying configurational density of states of a molecular system by combining information from several microcanonical molecular dynamics or Monte Carlo simulations at different energies. This method is based on Jaynes' Maximum Entropy formalism (MaxEnt) for Bayesian statistical inference under known expectation values. We present results of its application to measure thermodynamic entropy and free energy differences in embedded-atom models of metals.

1. Introduction

The Maximum Entropy (MaxEnt) principle, proposed by Jaynes in 1957 [1] and widely used in Bayesian probability, allows the construction of the most unbiased probabilistic models that reproduce certain information. Recently, Caticha [2] has proposed a Maximum Relative Entropy principle to update a probabilistic model under known information from a previous state of knowledge. In this work we apply this idea to the microcanonical distribution of configurational degrees of freedom, in order to update a previous guess of the configurational density of states (CDOS) with information from several microcanonical simulations at different energies.

2. Microcanonical distribution

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 Hamiltonian

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

The probability of the system having phase space coordinates $(\mathbf{r}, \mathbf{p})$ at fixed total energy E is given by [3, 4]

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

where

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

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 [5, 6, 7, 8]. The probability distribution function for the configurational degrees of freedom takes the form

$$P(\mathbf{r}; E) = \frac{1}{\eta(E)} \Theta(E - \Phi(\mathbf{r}))\sqrt{E - \Phi(\mathbf{r})}^{3N-2}, \tag{4}$$

where

$$\eta(E) = \int d\mathbf{r}\,\Theta(E - \Phi(\mathbf{r}))\sqrt{E - \Phi(\mathbf{r})}^{3N-2} \tag{5}$$

is proportional to $\Omega(E)$ and $\Theta(x)$ is Heaviside's step function.

Using Eq. 4 we can define the microcanonical expectation value of any configurational quantity $A(\mathbf{r})$ as

$$\langle A \rangle_E = \frac{1}{\eta(E)} \int d\mathbf{r}\,\Theta(E - \Phi(\mathbf{r}))\sqrt{E - \Phi(\mathbf{r})}^{3N-2} A(\mathbf{r}). \tag{6}$$

3. Determination of the Density of States
From Eq. 6, it can be deduced that

$$P(\phi; E) = \langle \delta(\Phi(\mathbf{r}) - \phi) \rangle = \frac{1}{\eta(E)} \Theta(E - \phi)\sqrt{E - \phi}^{3N-2}\mathcal{D}(\phi) \tag{7}$$

where

$$\mathcal{D}(\phi) = \int d\mathbf{r}\,\delta(\Phi(\mathbf{r}) - \phi) \tag{8}$$

is the configurational density of states (CDOS). If we have access to $\mathcal{D}(\phi)$ we can compute the expectation of any function of ϕ at an arbitrary energy E as

$$\langle A(\Phi) \rangle_E = \frac{1}{\eta(E)} \int_{\phi_0}^{E} d\phi\,\mathcal{D}(\phi)\sqrt{E - \phi}^{3N-2} A(\phi). \tag{9}$$

Our aim is to reconstruct $\mathcal{D}(\phi)$ from several known configurational averages at different energies. Suppose we have a prior estimate of the density of states, $\mathcal{D}_0(\phi)$ and incorporate knowledge of the following expectation value

$$\langle f(\Phi) \rangle_E = F(E), \tag{10}$$

then the most unbiased estimate of $\mathcal{D}(\phi)$ is obtained by maximization of the relative entropy

$$S[\mathcal{D}, \mathcal{D}_0] = -\int d\phi\,P(\phi; E) \ln\left(\frac{P(\phi; E)}{P_0(\phi; E)}\right) \tag{11}$$

under the constraint given in Eq. 10, where P and P_0 are the probability density functions using $\mathcal{D}$ and $\mathcal{D}_0$, respectively. This leads to the following updating rule

$$\mathcal{D}(\phi) = \mathcal{D}_0(\phi) \exp(\lambda f(\phi)), \tag{12}$$

where λ is a Lagrange multiplier to be determined by imposing the validity of the constraint itself, condition which can be written as

$$\frac{\partial}{\partial \lambda} \ln Z(\lambda) = F(E), \tag{13}$$

where

$$Z(\lambda) = \int_{\phi_0}^{E} d\phi \sqrt{E-\phi}^{3N-2} \mathcal{D}_0(\phi) \exp(\lambda f(\phi)). \tag{14}$$

Now, consider the case $f(\phi) = \Theta(b-\phi)\Theta(\phi-a)$, where a and b form an arbitrary interval so that $f(\phi) = 1$ if $a < \phi < b$, and $f(\phi) = 0$ otherwise. Then, $F(E)$ is just the probability $P(a < \Phi < b|E)$, that is, the probability of $\Phi(\mathbf{x})$ falling into the interval $[a, b]$. The normalization constant $Z(\lambda)$ is given by

$$Z(\lambda) = G(\phi_0, a) + G(b, E) + \exp(\lambda)G(a, b) \tag{15}$$

where

$$G(x, y) = \int_{x}^{y} d\phi \sqrt{E-\phi}^{3N-2} \mathcal{D}_0(\phi). \tag{16}$$

Eq. 13 thus connects λ with $P(a < \Phi < b|E)$ in the following form,

$$P(a < \Phi < b|E)\Big(G(\phi_0, a) + G(b, E) + \exp(\lambda)G(a, b)\Big) = \exp(\lambda)G(a, b), \tag{17}$$

therefore

$$\exp(\lambda) = \frac{P(a < \Phi < b|E)}{1 - P(a < \Phi < b|E)} \frac{(G(\phi_0, a) + G(b, E))}{G(a, b)}. \tag{18}$$

Consider now a discretization of ϕ in n intervals, $\phi = i\Delta\phi$, where $\Delta\phi = (E - \phi_0)/n$, and i an integer index between 0 and $n - 1$ (thus the condition $\phi < E$ is imposed implicitly, as $k < n$). To further simplify, we measure ϕ so that $\phi_0 = 0$ and $\Delta\phi = 1$. We can then approximate, for sufficiently large n,

$$G(a, b) = \sum_{i=a}^{b} \sqrt{E-i}^{3N-2} d_i^{(0)} \tag{19}$$

where $d_i^{(0)} = \mathcal{D}_0(i)$. Taking $a = k$ and $b = k + 1$, we have

$$d_k = \frac{N_k(E)}{N - N_k(E)} \frac{\sum_{i \neq k} \sqrt{E-i}^{3N-2} d_i^{(0)}}{\sqrt{E-k}^{3N-2}}. \tag{20}$$

where $N_k(E)$ is a histogram of potential energies at total energy E.

This is a relatively simple rule for incorporating information from a microcanonical simulation at total energy E into a prior guess of a discretized CDOS. The only input needed from the simulation is the histogram $N_k(E)$. This updating rule is guaranteed to converge: when it does $(d_k = d_k^{(0)})$, we have

$$P_k(E) = \frac{N_k(E)}{N} = \frac{\sqrt{E-k}^{3N-2} d_k}{\sum_{i=0}^{n-1} \sqrt{E-i}^{3N-2} d_i}, \tag{21}$$

which is just a discretized version of Eq. 7, and the denominator is an estimate of $\eta(E)$, the full (kinetic plus configurational) density of states.

In practice, we may start with a constant CDOS as initial guess, $d_k^{(0)} = 1$, and iteratively combine the information from several microcanonical simulations at different energies, each one only updating the CDOS for the potential energies actually observed.
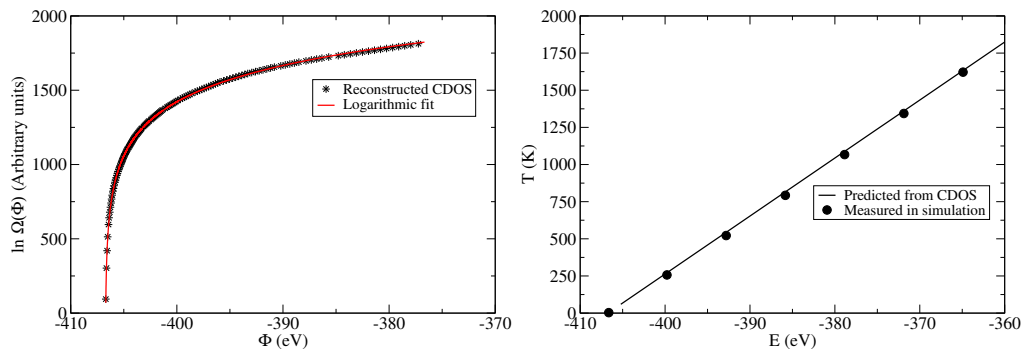
Figure 1. Left panel, reconstructed configurational density of states (CDOS) for Au, 108 atoms. Right panel, predicted caloric curve from CDOS and actual simulation values.

4. Results

Figure 1 (left panel) shows the CDOS computed using this procedure for a Au system composed of 108 atoms, simulated at 24 different energies (corresponding to applying initial kinetic energies between 6K and 6000K to the ideal face-centered cubic structure) via molecular dynamics with the Sutton-Chen potential [9]. This CDOS agrees remarkably with a simple model

$$\mathcal{D}(\phi) = \Big(a(\phi - \phi_0) + 1\Big)^b, \tag{22}$$

with fitted parameters a =43.764 eV^{-1}, b =134.297, and the energy of the ideal crystalline structure ϕ_0 =-406.715 eV. The right panel of figure 1 shows the predicted values of temperature as a function of total energy, together with the measured values from several simulations. These predicted temperatures are derived from the CDOS by computing, according to Eq. 9, the expectation value

$$T = \Big\langle \frac{2(E - \Phi)}{3N} \Big\rangle_E. \tag{23}$$

5. Final Remarks

We have developed a method for obtaining the configurational density of states from microcanonical simulations, based on maximization of the relative configurational entropy under known expectation values. The formula (Eq. 20) resembles the histogram reweighting methods for the canonical ensemble [10].

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