1 Wang-Landau algorithm for systems interacting with an algebraic potential

One considers a system of N identical particles of mass m with positions $\mathbf{q}_i$ and momentum $\mathbf{p}_i$ with the Hamiltonian

$$\mathcal{H} = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m} + \mathcal{U}(\mathbf{q}_1, \mathbf{q}_2, \cdots, \mathbf{q}_n) \tag{1}$$

The Wang-Landau algorithm estimates the density of states of the potential energy $g(U, V)$ where V is the volume of the simulation box, up to a multiplicative constant.

$$g(U, V) = \int \prod_{i=1}^{N} d^3 q_i \delta(U - \mathcal{U}(\mathbf{q}_1, \mathbf{q}_2, \cdots, \mathbf{q}_n)) \tag{2}$$

1. Propose a Wang-Landau algorithm which allows one to compute the density of state $g(U, V)$. In particular, starting from a random configuration, how to compute the density of states $g(U, V)$ for a given volume V. Explain the role of the modification factor. Explain how is a trial configuration accepted or not.
2. In a canonical ensemble, the partition function is given by

$$Q(T, V) = \frac{1}{N! h^{3N}} \int \prod_{i=1}^{N} d^3 q_i \prod_{i=1}^{N} d^3 p_i \exp(-\mathcal{H}/k_b T) \tag{3}$$

   show that the partition function can be written as

$$Q(T, V) = \frac{1}{N! \Lambda^{3N}} Z(U, V) \tag{4}$$

   where Λ is a function of $m, k_B T$ and h and $Z(U, V)$ is a weighted integral of $g(U, V)$ to be determined.
3. By using the thermodynamic relations, show that the mean energy is expressed as

$$\langle E \rangle = \frac{3N k_B T}{2} + \frac{\int dU U g(U, V) e^{-U/k_B T}}{\int dU g(U, V) e^{-U/k_B T}} \tag{5}$$

4. Infer the expression of specific heat C_v as integrals over $g(U, V)$.
5. Justify that, even though for a Wang-Landau algorithm, the density of states is obtained up to a multiplicative constant, one can determine the thermodynamic quantities $\langle E \rangle$ and C_v.
6. Why cannot the pressure be obtained from a single Wang-Landau simulation at a fixed volume V ?

7. We now consider the microcanonical ensemble. The entropy is given by $S(E, V) = k_B \ln \Omega(E, V)$ where

$$\Omega(E, V) = \frac{1}{N!h^{3N}} \int \prod_{i=1}^{N} d^3p_i d^3q_i \delta(E - \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m} - \mathcal{U})) \tag{6}$$

By using the inverse Laplace representation of the δ function and integrating over the momentum p_i, show that

$$\Omega(E, V) = A \int \prod_{i=1}^{N} d^3q_i (E - \mathcal{U})^{3N/2-1} \theta(E - \mathcal{U}) \tag{7}$$

where A is a function which depends on h, N and m, to be determined.

8. By using the definition of the density of states $g(U, V)$, give the microcanonical entropy as an integral over $g(U, V)$.

We now consider systems where the potential energy within the simulation box obeys a scaling property

$$\mathcal{U}(L\mathbf{q}_1, L\mathbf{q}_2, \cdots, L\mathbf{q}_N) = L^\gamma \mathcal{U}(\mathbf{q}_1, \mathbf{q}_2, \cdots, \mathbf{q}_N) \tag{8}$$

9. Defining the reduced potential energy $\tilde{U} = U/L^\gamma$, and the associated density of states $\tilde{g}(\tilde{U})$ corresponding to a simulation in a unit volume, show by using Eq.(7) that

$$\Omega(E, V) = L^\delta \tilde{\Omega}(\tilde{E}) \tag{9}$$

where δ is a exponent to be determined and $\tilde{\Omega}(\tilde{E})$ the density of states of the system in a simulation box of unit volume.

10. Show that the microcanonical temperature can be written as

$$\frac{1}{T} = \frac{k_B}{L^\gamma} \frac{\partial \ln \tilde{\Omega}(\tilde{E})}{\partial \tilde{E}} \tag{10}$$

11. By using a thermodynamic relation and $V = L^3$, show that the equation of state PV/k_BT is a simple function of N, γ and $e = E/(Nk_BT)$.

12. Now, in the canonical ensemble, show that the partition function $Q(V, T)$ can be expressed as

$$Q(V, T) = L^\mu \tilde{Q}(\tilde{T}) \tag{11}$$

with

$$\tilde{Q}(\tilde{T}) = \frac{(2\pi m k_B \tilde{T})^{3N/2}}{N!h^{3N}} \int d\tilde{U} \tilde{g}(\tilde{U}) e^{-\tilde{U}/k_B\tilde{T}} \tag{12}$$

where $\tilde{T} = T/L^\gamma$ is the rescaled temperature, μ is an exponent to be determined

13. By using the thermodynamic relation, show that the equation of state $PV/(k_BT)$ is given as a function of N, γ and $e = \langle E \rangle/(Nk_BT)$.

14. Compare the equations of state obtained in the microcanonical and canonical ensembles. What happens in the large N limit ?

Glossary

— Thermodynamic relations

In a microcanonical ensemble

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_V$$

$$P = T\left(\frac{\partial S}{\partial V}\right)_E$$

In a canonical ensemble

$$P = -\left(\frac{\partial F}{\partial V}\right)_T$$