1 Optimizing the parallel tempering method

One considers a system of N identical point particles of mass m. The Hamiltonian of the system is given by

$$H = \sum_{i=1}^{N} \frac{\vec{p}_i^2}{2m} + V(\vec{x}^N) \tag{1}$$

where $V(\vec{x}^N)$ is the interaction potential, $\vec{p}_i$, the momentum of particle i, and $\vec{x}^N = (\vec{x}_1, \vec{x}_2, \cdots, \vec{x}_N)$ is a short-hand notation for the particle positions. In order to study the phase diagram, one performs a Monte Carlo simulation using the tempering method. It consists in performing simulation with M different boxes. Each box is in contact with a thermostat at the inverse temperature β_i. The inverse temperatures β_i are given by a increasing sequence $\beta_{i-1} < \beta_i < \beta_{i+1}$. The stochastic evolution of the system is given by two kinds of Markovian processes : single moves in each box using a Metropolis rule and particle swaps between two nearest neighbor boxes following also a Metropolis rule.

Let us denote the configurational integral of the canonical partition function as

$$Q(\beta) = \int d\vec{x}^N \exp\left(-\beta V(\vec{x}_N)\right) \tag{2}$$

where $d\vec{x}^N = \prod_{i=1}^{N} d\vec{x}_i$.

1. Express the joint probability distribution density of the particles $P(\beta, \beta', \vec{x}^N, \vec{x}'^N)$ of two boxes at the inverse temperature β and β' as a function of $Q(\beta)$ $Q(\beta')$, β, β' $V(\vec{x}_i)$ and $V(\vec{x}'_i)$.
2. Defining $P_a(\beta, \beta')$ the acceptance probability for particle swaps between neighboring boxes at the inverse temperatures β and β', justify that

$$P_a(\beta, \beta') = \iint d\vec{x}^N d\vec{x'}^N P(\beta, \beta', \vec{x}^N, \vec{x'}^N) \mathrm{Min}\left(1, \exp\left((\beta' - \beta)(V(\vec{x'}_N) - V(\vec{x}_N))\right)\right) \tag{3}$$

3. Justify that $P_a(\beta, \beta') = P_a(\beta', \beta)$
4. For the sake of simplicity, one now assumes that $\beta' > \beta$, show that

$$\mathrm{Min}\left(1, \exp\left([\beta' - \beta][\mathrm{V}(\tilde{\mathrm{x}}'_\mathrm{N}) - \mathrm{V}(\tilde{\mathrm{x}}_\mathrm{N})]\right)\right) = \exp\left(\frac{(\beta' - \beta)}{2}(\mathrm{V}(\tilde{\mathrm{x}}'_\mathrm{N}) - \mathrm{V}(\tilde{\mathrm{x}}_\mathrm{N}))\right)$$
$$\exp\left(-\frac{(\beta' - \beta)}{2}|V(\vec{x'}_N) - V(\vec{x}_N)|\right) \tag{4}$$

5. Introducing the variables $R = \frac{\beta'}{\beta}$ and $\overline{\beta} = \frac{\beta+\beta'}{2}$, show that

$$P_a(\beta, \beta') = \frac{Q^2(\overline{\beta})}{Q(\beta)Q(\beta')} \iint d\vec{x}^N d\vec{x'}^N P(\overline{\beta}, \overline{\beta}, \vec{x}^N, \vec{x'}^N) \exp\left(-\frac{R-1}{R+1}\overline{\beta}|V(\vec{x'}_N) - V(\vec{x}_N)|\right) \tag{5}$$

One aims to obtain an asymptotic estimate of P_a when $\beta' - \beta \ll 1$,namely $R - 1 \ll 1$.

6. Using the thermodynamic relation $C_v(\beta) = -\beta^2 \frac{\partial^2 \beta F(\beta)}{\partial \beta^2}$ (where $F(\beta)$ is the excess free energy of the system), show that

$$\frac{Q^2(\overline{\beta})}{Q(\beta)Q(\beta')} = 1 - \left(\frac{R-1}{R+1}\right)^2 Cv(\overline{\beta}) + O(|R-1|^3) \tag{6}$$

where C_v is the specific heat of the system.

7. Show that

$$\iint d\vec{x}^N d\vec{x'}^N P(\overline{\beta}, \overline{\beta}, \vec{x}^N, \vec{x'}^N) \exp\left(-\frac{R-1}{R+1}\overline{\beta}|V(\vec{x'}_N) - V(\vec{x}_N)|\right) = 1 - \frac{R-1}{R+1}M(\overline{\beta}) + \left(\frac{R-1}{R+1}\right)^2 Cv(\overline{\beta}) + ... \tag{7}$$

where $M(\overline{\beta})$ is expressed as a mean average of $|V(\vec{x'}_N) - V(\vec{x}_N)|$.

8. Finally, by combining the above results, show that

$$P_a(\beta, \beta') = 1 - \frac{R-1}{R+1}M(\overline{\beta}) + O(|R-1|^3) \tag{8}$$

9. Using the Cauchy-Schwarz inequality $\langle|V(\vec{x'}_N) - V(\vec{x}_N)|\rangle^2 \leq \langle|V(\vec{x'}_N) - V(\vec{x}_N)|^2\rangle$, show that $M^2(\overline{\beta}) \leq 2C_V\overline{\beta})$

10. An optimal tempering Monte-Carlo method consists in having an equal acceptance between successive boxes. If the specific heat C_v (or M)is also constant in the range of $[\beta_{Max}, \beta_{Min}]$ show for N boxes that the inverse temperatures must be chosen as

$$R = \left(\frac{\beta_{max}}{\beta_{min}}\right)^{\frac{1}{N-1}} \tag{9}$$

and

$$\beta_i = R^{i-1}\beta_{min} \tag{10}$$

11. For the study of a first-order phase transition, can one assume a constant C_v ?