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

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

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

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

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 $V(\vec{x}'_i)$.

Solution: The joint probabilty of two boxes is given by

$$P(\beta, \beta', \vec{x}^N, \vec{x}'^N) = \frac{\exp\left(-\beta V(\vec{x}_N)\right)\exp\left(-\beta V(\vec{x}_N)\right)}{Q(\beta)Q(\beta')}$$

satisfying

$$\iint d\vec{x}^N d\vec{x'}^N P(\beta, \beta', \vec{x}^N, \vec{x}'^N) = 1$$

2. Defining $P_a(\beta, \beta')$ the acceptance probability for particle swaps between neighboring boxes at the inverse temperatures β and β', justify that

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

Solution: $\mathrm{Min}\left(1, \exp\left((\beta' - \beta)(V(\vec{x'}_N) - V(\vec{x}_N))\right)\right)$ is the probability of accepting a swap between two boxes. $P_a(\beta, \beta')$ is the average of this quantity over the equilibrium joint probability of two boxes.

3. Justify that $P_a(\beta, \beta') = P_a(\beta', \beta)$

> **Solution:** $P_a(\beta, \beta') = P_a(\beta', \beta)$ is symmetric by definition. Hopefully, because if a box accepts exchange with a second box, the acceptance of the second box must be identical !

4. For the sake of simplicity, one now assumes that $\beta' > \beta$, show that

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

> **Solution:** By using the property that $x/2 + |x|/2 = 0$ if $x < 0$ et $x/2 + |x|/2 = 1$ if $x > 0$, and taking the exponential of this property one obtains Eq.4

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

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

> **Solution:** One has $\beta - \beta = \frac{R-1}{R+1}\beta'$ which gives the exponential factor of Eq.5. Similarly
>
> $$\exp\left(\frac{(\beta' - \beta)}{2}(V(\vec{x'}_N) - V(\vec{x}_N))\right) P_\beta P_{\beta'} = P_{\overline{\beta'}} P_{\overline{\beta'}} Q^2(\overline{\beta})$$
>
> which gives Eq.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.

Solution: The expansion of the free energy gives

$$\beta F(\beta) = \overline{\beta} F(\overline{\beta}) + (\beta - \overline{\beta})\frac{\partial \beta F(\beta)}{\partial \beta} + \frac{1}{2}(\beta - \overline{\beta})^2 + \frac{\partial^2 \beta F(\beta)}{\partial \beta^2} + ...$$

By using $\beta F = -\ln(Q(\beta)$, one obtains Eq.6

7. Show that

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

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

Solution: Expanding the exponential up to the second order in $\frac{R-1}{R+1}$ gives Eq.7

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

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

Solution: The ratio of the two quantities cancels the second term of the expansion in $R-1$.

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 $M^2(\overline{\beta}) \leq 2C_V\overline{\beta})$

Solution: Expanding the righ-hand side term of the inequality give $2C_v$ and shows 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

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

and

$$\beta_i = R^{i-1}\beta_{min} \quad (10)$$

Solution: If R is constant, one has $\beta_{i+1} = R\beta_i$.The geometric series has a constraint $\beta_{max} = R^{N-1}\beta_{min}$

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

Solution: Except when the critical exponent $\alpha < 0$ the specific heat has a huge variation close the phase transition, which explains that this assumption is not correct.