1 Heat Capacity – Energy Fluctuations

Given a system at temperature T_0, what is the probability, $p(E)$ of seeing energy E?

The energy will have a maximum at E^*, so expand $ln(E)$ about E^*:

$$ln(p(E)) = \ln(p(E^*)) + \frac{d(\ln(p(E)))}{dE}(E - E^*) + \frac{1}{2}\frac{d^2(\ln(p(E)))}{dE^2}(E - E^*)^2 \tag{1}$$

We know the form of $p(E)$ is $\frac{g(E)e^{-\beta E}}{Q}$ where $g(E)$ is the multiplicity of the energy E, β is the inverse temperature, and Q is the partition function. So,

$$\ln(p(E)) = \ln\left(\frac{g(E)}{Q}\right) - \beta E$$

$$\frac{d(\ln(p(E)))}{dE} = \frac{d}{dE}\ln(g(E)) - \beta = \frac{d}{dE}\left(\frac{S(E)}{k_\mathrm{B}}\right) - \beta = \frac{1}{k_\mathrm{B}T(E)} - \frac{1}{k_\mathrm{B}T_0}$$

The first derivative evaluated at $T(E) = T_0$ gives 0. Taking the second derivative,

$$\frac{d^2(\ln(p(E)))}{dE^2} = \frac{d}{dE}\left(\frac{1}{k_\mathrm{B}T(E)} - \beta\right) = \frac{-1}{k_\mathrm{B}(T(E))^2}\frac{dT}{dE} = \frac{-1}{k_\mathrm{B}(T(E))^2 c_V}$$

Evaluating the second derivative at $T(E) = T_0$ and plugging both results into the original Taylor series yields:

$$\ln(p(E)) = \ln(p(E^*)) + \frac{-1}{2k_\mathrm{B}T_0^2 c_V}(E - E^*)^2 + \mathcal{O}((E - E^*)^3)$$

$$p(E) = p(E^*)\ \exp\left(\frac{-(E - E^*)^2}{2k_\mathrm{B}T_0^2 c_V}\right)$$

where $p(E^*)$ is a normalization constant. This is a normal distribution whose variance is $2k_\mathrm{B}T_0^2 c_V$. Therefore,

$$c_V = \frac{\mathrm{Var(E)}}{k_\mathrm{B}T_0^2} \tag{2}$$

2 IFC2 from System Energy (Pair Potential)

The total potential energy of an atomic system governed by a pair potential is given by:

$$U = \sum_i \sum_{j>i} \phi(r_{ij})$$

Therefore, the second order force constants are:

$$\frac{\partial^2 U}{\partial r_i^\alpha \partial r_j^\beta} = \frac{\partial^2}{\partial r_i^\alpha \partial r_j^\beta}\sum_n \sum_{m>n} \phi(r_{nm})$$

The sum indices are changed from the conventional notation to avoid confusion with the i and j which denote which atoms the derivatives are with respect to. This derivative will only be non-zero in the case where (n,m) = (i,j) so:

$$\frac{\partial^2 U}{\partial r_i^\alpha \partial r_j^\beta} = \frac{\partial^2 \phi(r_{ij})}{\partial r_i^\alpha \partial r_j^\beta}$$

This is only the case when $i \neq j$, to find the force constants when $i = j$

3 Pair Potential Derivative (2nd Order)

Given a pair potential $\phi(r_{ij})$ where r_{ij} is the distance between particles r_i and r_j the second derivative w.r.t atomic displacements is:

$$\frac{\partial^2 \phi(r_{ij})}{\partial u_i^\alpha \partial u_j^\beta} = \frac{\partial^2 \phi(r_{ij})}{\partial r_i^\alpha \partial r_j^\beta}\frac{\partial r_i^\alpha}{\partial u_i^\alpha}\frac{\partial r_j^\beta}{\partial u_j^\beta} = \frac{\partial^2 \phi(r_{ij})}{\partial r_i^\alpha \partial r_j^\beta}$$

where u_i^α is the displacement of atom i in the α direction and r_i^α is the α coordinate of atom i.

Therefore,

$$\frac{\partial^2 \phi(r_{ij})}{\partial r_i^\alpha \partial r_j \beta} = \frac{\partial}{\partial r_i^\alpha}\left(\frac{\partial \phi(r_{ij})}{\partial r_j^\beta}\right) = \frac{\partial}{\partial r_i^\alpha}\left(\frac{\partial \phi(r_{ij})}{\partial r_{ij}}\frac{\partial r_{ij}}{\partial r_j^\beta}\right) = \frac{\partial^2 \phi(r_{ij})}{\partial r_i^\alpha \partial r_{ij}}\frac{\partial r_{ij}}{\partial r_j^\beta} + \frac{\partial \phi(r_{ij})}{\partial r_{ij}}\frac{\partial^2 r_{ij}}{\partial r_i^\alpha \partial r_j \beta} =$$

$$\frac{\partial^2 \phi(r_{ij})}{\partial r_{ij}^2}\frac{\partial r_{ij}}{\partial r_i^\alpha}\frac{\partial r_{ij}}{\partial r_j^\beta} + \frac{\partial \phi(r_{ij})}{\partial r_{ij}}\frac{\partial^2 r_{ij}}{\partial r_i^\alpha \partial r_j \beta} = \phi''(r_{ij})\frac{\partial r_{ij}}{\partial r_i^\alpha}\frac{\partial r_{ij}}{\partial r_j^\beta} + \phi'(r_{ij})\frac{\partial^2 r_{ij}}{\partial r_i^\alpha \partial r_j \beta}$$

r_{ij} is simply the distance between two particles:

$$r_{ij} = \sqrt{(r_i^\alpha - r_j^\alpha)^2 + (r_i^\beta - r_j^\beta)^2 + (r_i^\gamma - r_j^\gamma)^2}$$

$$\frac{\partial r_{ij}}{\partial r_j^\beta} = \frac{r_i^\beta - r_j^\beta}{r_{ij}}$$

$$\frac{\partial^2 r_{ij}}{\partial r_i^\alpha \partial r_j^\beta} = \frac{\partial}{\partial r_i^\alpha}\frac{(r_i^\beta - r_j^\beta)}{r_{ij}} = \frac{\delta_{\alpha\beta}}{r_{ij}} - \frac{(r_i^\alpha - r_j^\alpha)(r_i^\beta - r_j^\beta)}{r_{ij}^3}$$

where $\delta_{\alpha\beta}$ is the Kronecker delta to handle the case when $\alpha = \beta$. Plugging this back into the original equation we get,

$$\frac{\partial^2 \phi(r_{ij})}{\partial r_i^\alpha \partial r_j \beta} = \phi''(r_{ij})\frac{(r_i^\alpha - r_j^\alpha)(r_i^\beta - r_j^\beta)}{r_{ij}^2} + \phi'(r_{ij})\left(\frac{\delta_{\alpha\beta}}{r_{ij}} - \frac{(r_i^\alpha - r_j^\alpha)(r_i^\beta - r_j^\beta)}{r_{ij}^3}\right)$$

$$= \frac{(r_i^\alpha - r_j^\alpha)(r_i^\beta - r_j^\beta)}{r_{ij}^2}\left(\phi''(r_{ij}) - \frac{\phi'(r_{ij})}{r_{ij}}\right) + \phi'(r_{ij})\frac{\delta_{\alpha\beta}}{r_{ij}}$$

4 Force Constant → Modal Coupling Constant

The third order term in the Taylor Effective Potential is given as

$$U_3 = \frac{1}{3!}\sum_{\substack{ijk\\ \alpha\beta\gamma}} \Psi_{ijk}^{\alpha\beta\gamma} u_i^\alpha u_j^\beta u_k^\gamma \tag{3}$$

To convert to normal mode coordinates we can substitute:

$$u_i^\alpha = \frac{1}{\sqrt{m_i}}\sum_n q_n e_{ni}^\alpha$$

$$U_3 = \frac{1}{3!}\sum_{\substack{ijk\\ \alpha\beta\gamma}} \Psi_{ijk}^{\alpha\beta\gamma} \frac{1}{\sqrt{m_i}}\sum_n q_n e_{ni}^\alpha \frac{1}{\sqrt{m_j}}\sum_m q_m e_{mj}^\beta \frac{1}{\sqrt{m_k}}\sum_l q_l e_{lk}^\gamma$$

$$U_3 = \frac{1}{3!}\sum_{nml}\sum_{\substack{ijk\\ \alpha\beta\gamma}} \Psi_{ijk}^{\alpha\beta\gamma}\frac{e_{ni}^\alpha e_{mj}^\beta e_{lk}^\gamma q_n q_m q_l}{\sqrt{m_i m_j m_k}}$$

$$U_3 = \sum_{nml} K_{nml} q_n q_m q_l$$

$$K_{nml} = \sum_{\substack{ijk\\ \alpha\beta\gamma}} \Psi_{ijk}^{\alpha\beta\gamma}\frac{e_{ni}^\alpha e_{mj}^\beta e_{lk}^\gamma}{\sqrt{m_i m_j m_k}} \tag{4}$$

5 Dynamical Matrix

6 Equipartition Theorem

7 SHAKE

This derivation follows the steps in this paper (without skipping algebra).

Given a set of N_c holonomic constraints for a molecule:

$$\sigma_k(r_i) = r_{k_1k_2}^2 - d_{k_1k_2}^2 = 0, k = 1, ...N_c$$

where r_i is the position vector for atom i, $r_{k_1k_2}$ is the distance between atoms k_1 and k_2 in constraint k and $d_{k_1k_2}$ is the constraint distance. The equations of motion become:

$$m_i\frac{\partial^2 r_i(t)}{\partial t^2} = -\frac{\partial}{\partial r_i}\left(V(r_i) + \sum_{k=1}^{N_c}\lambda_k(t)\sigma_k(r_i)\right)$$

where $\lambda_k(t)$ is the time dependent Lagrange multiplier for constraint k. Define, f_i^{uc} as the unconstrained force acting on atom i and f_i^c as the force on atom i due to the constraints.

$$f_i^{uc} = -\frac{\partial V(r(i))}{\partial r_i}$$

$$f_i^c = -\sum_{k=1}^{N_c}\lambda_k(t)\frac{\partial \sigma_k(r_i(t))}{\partial r_i(t)} = -2\sum_{k=1}^{N_c}\lambda_k(t)(\delta_{i,k_1} - \delta_{i,k_2})r_{k_1k_2}(t)$$

The new coordinates which satisfy the constraints will be given by:

Is this step update scheme agnostic, or can the dt^2/m change w/ scheme??

$$r_i^c(t_\Delta + t) = r_i^{uc}(t + \Delta t) + \frac{\Delta t^2}{m_i}f_i^c(t)$$

These new coordinates must satisfy the original set of constraints $\sigma_k(r_i)$. Therefore, plugging the previous line into the constraint equation we get:

$$\left(\left[(r^{uc}_{k_1}(t+\Delta t)+\frac{\Delta t^2}{m_{k_1}}f^c_{k_1}(t)\right]-\left[(r^{uc}_{k_2}(t+\Delta t^2)+\frac{\Delta t^2}{m_{k_2}}f^c_{k_2}(t)\right]\right)^2-d^2_{k_1k_2}=0$$

$$\left[r^{uc}_{k_1k_2}(t+\Delta t)+\frac{\Delta t^2}{m_{k_1}}f^c_{k_1}(t)-\frac{\Delta t^2}{m_{k_2}}f^c_{k_2}(t)\right]^2-d^2_{k_1k_2}=0$$

This equation must be satisfied for all N_c constraints. As a notational note, the equation above represents the k^{th} constraint between atoms k_1 and k_2. To use this equation to solve for the Lagrange multipliers λ_k we must plug in the equation for the constraint forces acting on atom i, f^c_i, which is derived above.

$$\left[r^{uc}_{k_1k_2}(t+\Delta t)-2\frac{\Delta t^2}{m_{k_1}}\left(\sum_{k'=1}^{N_c}\lambda_{k'}(t)(\delta_{k_1,k'_1}-\delta_{k'_1,k_2})r_{k'_1k'_2}(t)\right)+2\frac{\Delta t^2}{m_{k_2}}\left(\sum_{k'=1}^{N_c}\lambda_{k'}(t)(\delta_{k_2,k'_1}-\delta_{k_2,k'_2})r_{k'_1k'_2}(t)\right)\right]^2-d^2_{k_1k_2}=0$$

$$\left[r^{uc}_{k_1k_2}(t+\Delta t)-2\Delta t^2\left(\sum_{k'=1}^{N_c}\lambda_{k'}(t)r_{k'_1k'_2}(t)*\left(\frac{(\delta_{k_1,k'_1}-\delta_{k'_1,k_2})}{m_{k_1}}-\frac{(\delta_{k_2,k'_1}-\delta_{k_2,k'_2})}{m_{k_2}}\right)\right)\right]^2-d^2_{k_1k_2}=0$$

The k' notation was introduced in the sum to avoid confusion with the non-prime k indices which correspond to constraint k and not an index of the sum. Again there are one of these equations for every constraint k between atoms k_1 and k_2 which leads to a system of N_c equations that can be solved for λ_k. These equations are solved approximately by ignoring terms quadratic in λ. To see the quadratic part we will multiply out the previous equation:

$$\left(r^{uc}_{k_1k_2}(t+\Delta t)\right)^2-4\Delta t^2r^{uc}_{k_1k_2}(t+\Delta t)\left(\sum_{k'=1}^{N_c}\lambda_{k'}(t)r_{k'_1k'_2}(t)*\left(\frac{(\delta_{k_1,k'_1}-\delta_{k'_1,k_2})}{m_{k_1}}-\frac{(\delta_{k_2,k'_1}-\delta_{k_2,k'_2})}{m_{k_2}}\right)\right)+$$
$$\left(2\Delta t^2\sum_{k'=1}^{N_c}\lambda_{k'}(t)r_{k'_1k'_2}(t)*\left(\frac{(\delta_{k_1,k'_1}-\delta_{k'_1,k_2})}{m_{k_1}}-\frac{(\delta_{k_2,k'_1}-\delta_{k_2,k'_2})}{m_{k_2}}\right)\right)^2=d^2_{k_1k_2}$$

Ignoring the last term which is quadratic in λ we find that:

$$\frac{\left(r^{uc}_{k_1k_2}(t+\Delta t)\right)^2-d^2_{k_1k_2}}{4\Delta t^2}=r^{uc}_{k_1k_2}(t+\Delta t)\left(\sum_{k'=1}^{N_c}\lambda_{k'}(t)r_{k'_1k'_2}(t)*\left(\frac{(\delta_{k'_1,k_1}-\delta_{k'_1,k_2})}{m_{k_1}}-\frac{(\delta_{k_2,k'_1}-\delta_{k_2,k'_2})}{m_{k_2}}\right)\right)$$

Recall that this equation corresponds to constraint k between atoms k_1 and k_2. Now that our system is linear we can pose it as a matrix-vector product: $[A]\overrightarrow{\lambda}=\overrightarrow{c}$. Each row of the matrix A is defined by the RHS of the above equation. Likewise c is defined by the LHS.

$$A_{kk'}=r^{uc}_{k_1k_2}(t+\Delta t)\cdot r_{k'_1k'_2}(t)\left(\frac{(\delta_{k'_1,k_1}-\delta_{k'_1,k_2})}{m_{k_1}}-\frac{(\delta_{k_2,k'_1}-\delta_{k_2,k'_2})}{m_{k_2}}\right)$$

$$c_k=\frac{\left(r^{uc}_{k_1k_2}(t+\Delta t)\right)^2-d^2_{k_1k_2}}{4\Delta t^2}$$

This formulation of SHAKE differs slightly from the original paper which assumed that all constraints were independent yielding a decoupled A matrix. Now the A matrix is dense and the resulting forces between constraints are accounted for. The solution to this equation can be solved by simple matrix inversion, Cramer's rule, LU factorization and LDL factorization. The paper linked above goes into detail about the computational benefits and drawbacks of each approach. Since the constraints might not be satisfied immediately, the positions and Lagrange multipliers are calculated in an iterative process until the constraints are satisfied.

Still don't get why iterating on the linearized solutions is guranteed to converge to 0???

8 RATTLE

In schemes which also integrate the velocities (e.g. Velocity Verlet) the velocities must also satisfy the contraints:

$$\frac{d\sigma_k(r_i(t))}{dt}=\frac{\partial\sigma_k(r_i(t))}{\partial r_i(t)}\frac{\partial r_i(t)}{\partial t}=r_{k_1k_2}(t)\cdot v_{k_1k_2}(t)=0$$

In the Velocity Verlet scheme the constrained velocity update is given by:

$$v^c_i(t+\Delta t)=v^c_i(t)+\frac{\Delta t}{m_i}\left(f^{uc}_i(t)+f^c_i(t)+f^{uc}_i(t+\Delta t)+f^c_i(t+\Delta t)\right)$$

Let,

$$v^0_i(t)=v^c_i(t)+\frac{\Delta t}{m_i}(f^{uc}_i(t)+f^c_i(t))$$

The only unknown in the equation for the constrainted velocities is $f_i^c(t+\Delta t)$ as $f_i^c(t)$ can be calculated from the Lagrange multiplers found by SHAKE. These constrained velocities must satisfy the constraints. Plugging $v_i^c(t+\Delta t)$ into the constraint equation allows us to solve for $f_i^c(t+\Delta t)$.

$$r_{k_1k_2}(t+\Delta t)\cdot v_{k_1k_2}(t+\Delta t)=0$$

$$r_{k_1k_2}(t+\Delta t)\cdot\left[v_{k_1}^0(t)+\frac{\Delta t}{m_i}\left(f_{k1}^{uc}(t+\Delta t)+f_{k1}^c(t+\Delta t)\right)\right]-\left[v_{k_2}^0(t)+\frac{\Delta t}{m_i}\left(f_{k2}^{uc}(t+\Delta t)+f_{k2}^c(t+\Delta t)\right)\right]=0$$

$$r_{k_1k_2}(t+\Delta t)\cdot\left[v_{k_1k_2}^0(t)+\frac{\Delta t}{m_{k_1}}\left(f_{k1}^{uc}(t+\Delta t)+f_{k1}^c(t+\Delta t)\right)-\frac{\Delta t}{m_{k_2}}\left(f_{k2}^{uc}(t+\Delta t)+f_{k2}^c(t+\Delta t)\right)\right]=0$$

$$r_{k_1k_2}(t+\Delta t)\left[\Delta t v_{k_1k_2}^0(t)+\frac{\Delta t^2 f_{k_1}^{uc}(t+\Delta t)}{m_{k_1}}-\frac{\Delta t^2 f_{k_2}^{uc}(t+\Delta t)}{m_{k_2}}\right]=$$
$$-\Delta t^2 r_{k_1k_2}(t+\Delta t)\left[\frac{f_{k_1}^c(t+\Delta t)}{m_{k_1}}-\frac{f_{k_2}^c(t+\Delta t)}{m_{k_2}}\right]$$

$$r_{k_1k_2}(t+\Delta t)\left[\Delta t v_{k_1k_2}^0(t)+\frac{\Delta t^2 f_{k_1}^{uc}(t+\Delta t)}{m_{k_1}}-\frac{\Delta t^2 f_{k_2}^{uc}(t+\Delta t)}{m_{k_2}}\right]=$$
$$2\Delta t^2 r_{k_1k_2}(t+\Delta t)\sum_{k'=1}^{N_c}\eta_{k'}(t)r_{k_1'k_2'}(t)\left(\frac{(\delta_{k_1,k_1'}-\delta_{k_1',k_2})}{m_{k_1}}-\frac{(\delta_{k_2,k_1'}-\delta_{k_2,k_2'})}{m_{k_2}}\right)$$

$$r_{k_1k_2}(t+\Delta t)\left[\Delta t v_{k_1k_2}^0(t)+\frac{\Delta t^2 f_{k_1}^{uc}(t+\Delta t)}{m_{k_1}}-\frac{\Delta t^2 f_{k_2}^{uc}(t+\Delta t)}{m_{k_2}}\right]=$$
$$4\Delta t^2 r_{k_1k_2}(t+\Delta t)\sum_{k'=1}^{N_c}\eta_{k'}(t+\Delta t)r_{k_1'k_2'}(t+\Delta t)\left(\frac{(\delta_{k_1,k_1'}-\delta_{k_1',k_2})}{m_{k_1}}-\frac{(\delta_{k_2,k_1'}-\delta_{k_2,k_2'})}{m_{k_2}}\right))$$

η_k is introduced as a second set of Lagrange multipliers for the velocity constraints. Again the prime indices correspond to sum index and the non-prime indices refer to the specific constraint this equation is for. Re-arranging this equation we find:

$$\frac{1}{4\Delta t^2}r_{k_1k_2}(t+\Delta t)\left[\Delta t v_{k_1k_2}^0(t)+\frac{\Delta t^2 f_{k_1}^{uc}(t+\Delta t)}{m_{k_1}}-\frac{\Delta t^2 f_{k_2}^{uc}(t+\Delta t)}{m_{k_2}}\right]=$$
$$r_{k_1k_2}(t+\Delta t)\sum_{k'=1}^{N_c}\eta_{k'}(t+\Delta t)r_{k_1'k_2'}(t+\Delta t)\left(\frac{(\delta_{k_1,k_1'}-\delta_{k_1',k_2})}{m_{k_1}}-\frac{(\delta_{k_2,k_1'}-\delta_{k_2,k_2'})}{m_{k_2}}\right))$$

Recognize this as the same matrix form from SHAKE but at time $t+\Delta t$ (this is for different constraints, cannot use η as λ for next SHAKE iteration). This equation is linear and can be solved for η_k and subsequently $v_i^c(t+\Delta t)$.