Computational biophysics

Protein's geometry

Centre of mass $\vec{R}_{cm} = \frac{\sum_{i=1}^{N} m_i \vec{r}_i}{\sum_{i=1}^{N} m_i}$ $\quad RMSD(t) = \sqrt{\frac{1}{N}\sum_{i=1}^{N}(\vec{r}_i(t) - \vec{r}_i(0))^2}$

Radius of gyration $r_g = \sqrt{\frac{\sum_{i=1}^{N} m_i(\vec{r}_i - \vec{R}_{cm})^2}{\sum_{i=1}^{N} m_i}}$ $\quad RMSF_i = \sqrt{\langle \Delta r_i^2 \rangle} = \sqrt{\frac{1}{M}\sum_{f=1}^{M}(\vec{r}_{i,f} - \langle \vec{r}_i \rangle)^2}$

$B_i = \frac{8\pi^2}{3} RMSF_i^2$

Semi-empirical force fields

Bond stretching

Harmonic $U(r_{AB}) = \frac{1}{2}k_{AB}(r_{AB} - r_{AB,eq})^2$

Anarmonic $U(r_{AB}) = \frac{1}{2}\left[k_{AB} + k_{AB}^{(3)}(r_{AB} - r_{AB,eq})\right](r_{AB} - r_{AB,eq})^2$

Quartic correction $U(r_{AB}) = \frac{1}{2}\left[k_{AB} + k_{AB}^{(3)}(r_{AB} - r_{AB,eq}) + k_{AB}^{(4)}(r_{AB} - r_{AB,eq})^2\right] \cdot \cdot (r_{AB} - r_{AB,eq})^2$

Morse $U(r_{AB}) = D_{AB}\left[1 - e^{-\alpha_{AB}(r_{AB} - r_{AB,eq}^2)}\right]$

Valence angle bending

Potential $U(\theta_{ABC}) = \frac{1}{2}[k_{ABC} + k_{ABC}^{(3)}(\theta_{ABC} - \theta_{ABC,eq}) + k_{ABC}^{(4)}(\theta_{ABC} - \theta_{ABC,eq})^2 + \cdots](\theta_{ABC} - \theta_{ABC,eq})^2$

Fourier $U(\theta_{ABC}) = \sum_{\{j\}_{ABC}} k_{j,ABC}^{fourier}[1 + \cos(j\theta_{ABC} + \psi_j)]$ $\quad k_{j,ABC}^{fourier} = \frac{2k_{ABC}^{harmonic}}{j^2}$

Torsions

Potential $U(\omega_{ABCD}) = \frac{1}{2}\sum_{\{j\}_{ABCD}} V_{j,ABCD}\left[1 + (-1)^{j+1}\cos(j\omega_{ABCD} + \psi_{j,ABCD})\right]$

Improper $U(\omega_{ABCD}) = \frac{1}{2}\sum_{\{j\}_{ABCD}} V_{j,ABCD}[1 + (-1)^{j+1}\cos(j\omega_{ABCD} + \psi_{j,ABCD})]$

Van der Waals

Lennard-Jones $U(r_{AB}) = 4\epsilon_{AB}\left[\left(\frac{\sigma_{AB}}{r_{AB}}\right)^{12} - \left(\frac{\sigma_{AB}}{r_{AB}}\right)^6\right]$

Morse $U(r_{AB}) = D_{AB}\left[1 - e^{-\alpha_{AB}(r_{AB} - r_{AB,eq}^2)}\right]^2$

Hill $U(r_{AB}) = \epsilon\left[\frac{6}{\beta_{AB}-6}e^{\beta_{AB}\frac{1-r_{AB}}{r_{AB}^*}} - \frac{\beta_{AB}}{\beta_{AB}-6}\left(\frac{r_{AB}^*}{r_{AB}}\right)^6\right]$

Electrostatic interactions

Distribution of charges $U_{AB} = \sum_A \sum_{B>A} \vec{M}^{(A)}\vec{V}^{(B)}$

Point like $U_{AB} = \frac{q_A q_B}{\epsilon_{AB} r_{AB}}$

Dipolar interactions $U_{AB/CD} = \frac{\mu_{AB}\mu_{CD}}{\epsilon_{AB/CD} r_{AB/CD}^3}(\cos\chi_{AB/CD} - 3\cos\alpha_{AB}\cos\alpha_{CD})$

Parameterization

Parameters $Z = \sqrt{\sum_i^{observables}\sum_j^{occurrences}\frac{(calc_{i,j} - expt_{i,j})^2}{w_i^2}}$

$\sigma_{AB} = \sigma_A + \sigma_B \qquad \epsilon_{AB} = \sqrt{\epsilon_A \epsilon_B}$

Classical mechanics

Newton's laws

$\vec{F} = m\vec{a} \qquad \vec{F}_{BA} = -\vec{F}_{AB}$

$\vec{v}(t) = \frac{d\vec{r}}{dt} \qquad \vec{a}(t) = \frac{d\vec{v}}{dt} = \frac{d^2\vec{r}}{dt^2} \qquad m\frac{d^2\vec{r}}{dt^2} = \vec{F}$

Force acting on atom $\vec{F}_i(\vec{r}_1, \ldots, \vec{r}_N, \dot{\vec{r}}_i) = \sum_{j\neq i}\vec{F}_{ij}(\vec{r}_i - \vec{r}_j) + \vec{F}^{(ext)}(\vec{r}_i, \dot{\vec{r}}_i)$

Bond stretching: $U = \frac{k_l}{2}(l - l^0)^2$

Bond bending: $U = \frac{k_\theta}{2}(\theta - \theta^0)^2$

Bond torsion: $U = k_\phi[1 + \cos(n\phi - \phi^0)]$

Van der Waals interactions: $U = \left[\frac{a_{ij}}{r_{ij}^{12}} - \frac{b_{ij}}{r_{ij}^6}\right]$

Electrostatic interactions: $U = \frac{332 q_i q_j}{\epsilon r_{ij}}$

$\vec{p}_i = m_i\vec{v}_i = m\dot{\vec{r}}_i \qquad \vec{F}_i = m_i\ddot{\vec{r}}_i = \dot{\vec{p}}_i$

$\vec{x}(t) = \{\vec{r}_1(t), \ldots, \vec{r}_N(t), \vec{p}_1(t), \ldots, \vec{p}_N(t)\}$

Lagrangian formulation

$\vec{F}_i(\vec{r}_1, \ldots, \vec{r}_N) = -\Delta_i U(\vec{r}_1, \ldots, \vec{r}_N)$

$W_{AB} = \int_A^B \vec{F}_i d\vec{l} = U_A - U_B = -\Delta U_{AB} \qquad \oint \vec{F}_i d\vec{l} = 0$

Kinetic energy $K(\dot{\vec{r}}_1, \ldots, \dot{\vec{r}}_N) = \frac{1}{2}\sum_i m_i \dot{\vec{r}}_i^2$

$\mathcal{L}(\vec{r}_1, \ldots, \vec{r}_N, \dot{\vec{r}}_1, \ldots, \dot{\vec{r}}_N) = K(\dot{\vec{r}}_1, \dot{\vec{r}}_N) - U(\vec{r}_1, \ldots, \vec{r}_N)$

Euler-Lagrange $\frac{d}{dt}\left(\frac{\partial\mathcal{L}}{\partial\dot{\vec{r}}_i}\right) - \frac{\partial\mathcal{L}}{\partial\vec{r}_i} = 0$

$E = \frac{1}{2}\sum_i m_i\dot{\vec{r}}_i^2 + U(\vec{r}_1, \ldots, \vec{r}_N)$

$quad\frac{dE}{dt} = 0$

Generalized coordinates

$q_\alpha = f_\alpha(\vec{r}_1, \ldots, \vec{r}_N) \qquad \alpha = 1, \ldots, 3N \qquad \vec{r}_i = \vec{g}_i(q_1, d\ldots, q_{3N}) \qquad i = 1, \ldots, N$

$\dot{\vec{r}}_i = \sum_{\alpha=1}^{3N}\frac{\partial\vec{r}_i}{\partial q_\alpha}\dot{q}_\alpha \qquad \mathcal{L}(q, \dot{q}) = \frac{1}{2}\sum_{\alpha=1}^{3N}\sum_{\beta=1}^{3N} G_{\alpha\beta}\dot{q}_\alpha\dot{q}_\beta - U(q_1, \ldots, q_{3N})$

Classical mechanics (contd)

Legendre transforms

$s = f'(x) \equiv g(x) \qquad f'(x) = g(x) = s \Rightarrow x = g^{-1}(s)$

$b(g^{-1}(s)) = f(g^{-1}(s)) - sg^{-1}(s) \equiv \tilde{f}(s) = f(x(s)) - sx(s)$

$\tilde{f}(s_1, \ldots, s_n) = f(x_1(s_1, \ldots, s_n), \ldots x_n(s_1, \ldots, s_n)) - \sum_i s_i x_i(s_1, \ldots, s_n)$

Hamiltonian formulation

$\mathcal{H}(\vec{r}_1, \ldots, \vec{r}_N, \vec{p}_1, \ldots, \vec{p}_N) = -\tilde{\mathcal{L}}(\vec{r}_1, \ldots, \vec{r}_N, \vec{p}_1, \ldots, \vec{p}_N)$

$\mathcal{H}(\vec{r}_1, \ldots, \vec{r}_N, \vec{p}_1, \ldots, \vec{p}_N) = \sum_{i=1}^N \frac{\vec{p}_i^2}{2m_i} + U(\vec{r}_1, \ldots, \vec{r}_N)$

$\mathcal{H}(q_1, \ldots, q_{3N}, p_1, \ldots, p_{3N}) = \frac{1}{2}\sum_\alpha\sum_\beta p_\alpha G_{\alpha\beta}^{-1}p_\beta + U(q_1, \ldots, q_{3N})$

Hamilton equations $\dot{q}_\alpha = \frac{\partial\mathcal{H}}{\partial p_\alpha} \qquad \dot{p}_\alpha = -\frac{\partial\mathcal{H}}{\partial q_\alpha} \qquad \frac{\mathcal{H}}{dt} = 0 \qquad \mathcal{H} = const$

Some properties

Conservation laws $\frac{da}{dt} = \frac{\partial a}{\partial x_t}\dot{x}(t) = \{a, \mathcal{H}\} = 0$

Incompressibility $\nabla_x\dot{x}(x) = 0$

Symplectic structure $M = J^T M J \qquad J_{kl} = \frac{\partial x_k(t)}{\partial x_l(0)}$

Theoretical foundations of statistical mechanics

Thermodynamics

Equilibrium $g(N, P, V, T) = 0$

State function $f(n, P, V, T)$

Reversible work $dW_{rev} = -PdV + \mu dN$

Heat $dQ_{rev} = CdT$

First law $\Delta E = \Delta Q + \Delta W$

Entropy $\Delta S = \int_1^2 \frac{dQ_{rev}}{T}$

The ensemble

Average $A = \frac{1}{Z}\sum_{\lambda=1}^N a(x_\lambda) \equiv \langle a \rangle$

Microstate $x_0 = (q_1(0), \ldots, q_{3N}(0), p_1(0), \ldots, p_{3N}(0))$

Phase space volume $dx_t = J(x_t; x_0)dx_0 \qquad \frac{dJ}{dt} = 0 \Rightarrow J(x_t; x_0) = 1 \Rightarrow dx_t = dx_0$

$f(x_t) : \int f(x)dx = 1 \wedge \frac{df(x_t, t)}{dt} = 0 \Rightarrow$

Distribution function $f(x_t, t)dx_t = f(x_0, 0)dx_0 \Rightarrow$

$\frac{\partial f(x, t)}{\partial t} + \{f(x, t), \mathcal{H}(x, t)\} = 0$

Equilibrium $A = \int a(x)f(x, t)dx \Rightarrow \frac{\partial f(x, t)}{\partial t} = 0 \wedge \{f(x, t), \mathcal{H}(x, t) = 0\} \Rightarrow$

$f(x) \propto \mathcal{F}(\mathcal{H}(x))$

$Z = \int dx\mathcal{F}(\mathcal{H}(x)) \Rightarrow f(x) = \frac{1}{Z}\mathcal{F}(\mathcal{H}(x))$

Microcanonical ensemble

State and distribution function

State function $dS = \frac{1}{T}dE + \frac{P}{T}dV - \frac{\mu}{T}dN$

$\left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{1}{T} \qquad \left(\frac{\partial S}{\partial V}\right)_{N,E} = \frac{P}{T} \qquad \left(\frac{\partial S}{\partial N}\right)_{V,N} = \frac{\mu}{T}$

Boltzmann relation $S(N, V, E) = k\ln\omega(N, V, E)$

$\Omega(N, V, E) = M_N\int d\vec{p}\int_{D(V)} d\vec{r}\delta(\mathcal{H}(\vec{r}, \vec{p}) - E)$

Distribution function $= M_N\int dx\delta(\mathcal{H}(x) - E)$

$M_N = \frac{E_0}{N!h^{3N}}$

$A = \langle a \rangle = \frac{M_N}{\Omega(N,V,E)}\int dxa(x)\delta(\mathcal{H}(x) - E) = \frac{\int dxa()\delta(\mathcal{H}(x) - E)}{\int dx\delta(\mathcal{H} - E)}$

$\left\langle x_i\frac{\partial\mathcal{H}}{\partial x_j}\right\rangle = \frac{M_N}{\Omega(N,V,E)}\frac{\partial}{\partial E}\int_{\mathcal{H}(x)<E} dxx_i\frac{\partial(\mathcal{H} - E)}{\partial x_j}$

Virial theorem

$\left\langle x_i\frac{\partial\mathcal{H}}{\partial x_j}\right\rangle = \delta_{ij}\frac{\Sigma(E)}{\frac{\partial\Sigma(E)}{\partial E}}$

$\Sigma(N, V, E) = \frac{1}{N!h^{3N}}\int dx\theta(E - \mathcal{H})$

$\Omega(N, V, E) = E_0\frac{\partial\Sigma(N,V,E)}{\partial E} \quad \left\langle x_i\frac{\partial\mathcal{H}}{\partial x_j}\right\rangle = \delta_{ij}\left(\frac{\ln\Sigma(E)}{\partial E}\right)^{-1}$

$S(N, V, E) = k\ln\Omega(N, V, E) \simeq k\ln\Sigma(N, V, E) = \tilde{S}(N, V, E)$

$\left\langle x_i\frac{\partial\mathcal{H}}{\partial x_j}\right\rangle \simeq \delta_{ij}\left(\frac{S(E)}{\partial E}\right)^{-1} = kT\delta_{ij}$

Thermal contact

$\Omega(N, V, E) = M_N\int dx\delta(\mathcal{H}_1(x_1) + \mathcal{H}_2(x_2) - E)$

$\Omega(N, V, E) = \int dE_1\Omega_1(N_1, V_1, E_1)\Omega_2(N_2, V_2, E - E_1)$

$S(N, V, E) = k\ln\Omega_1(N_1, V_1, \bar{E}_1) + k\ln\Omega_2(N_2, V_2, E - \bar{E}_1)$

$= S_1(N_1, V_1, \bar{E}_1) + S_2(N_2, V_2, E - \bar{E}_1)$

$T_1 = T_2$

Introduction to molecular dynamics

Verlet algorithm

$\vec{r}_i(t + \Delta t) = 2\vec{r}_i(t) - \vec{r}_i(t - \Delta t) + \frac{\Delta t^2}{m_i}\vec{F}_i(t)$

$\vec{v}_i(t + \Delta t) = \vec{v}_i(t) + \frac{\Delta t}{2m_i}\left[\vec{F}_i(t) + \vec{F}_i(t + \Delta t)\right]$

Initial conditions $f(v) = \sqrt{\frac{m}{2\pi kT}}e^{-\frac{mv^2}{2kT}} \qquad f(x) = \frac{1}{\sqrt{2\pi\sigma^2}}e^{-\frac{x^2}{2\sigma^2}}$

Introduction to molecular dynamics (contd)

Action integral

$Q \equiv \{q_1, \ldots, q_{3N}\} \qquad \dot{Q} \equiv \{\dot{q}_1, \ldots, \dot{q}_{3N}\}$

$A[Q] = \int_{t_1}^{t_2}\mathcal{L}(Q(t), \dot{Q}(t))dt$

$\delta Q(t_1) = \delta Q(t_2) = 0 \qquad \delta\dot{Q}(t_1) = \delta\dot{Q}(t_2) = 0$

$\delta A = \int_{\alpha=1}^{3N}\frac{\partial\mathcal{L}}{\partial\dot{q}_\alpha}\delta q_\alpha(t)\Big|_{t_1}^{t_2} dt + \int_{t_1}^{t_2}\sum_{\alpha=1}^{3N}\left[\frac{\partial\mathcal{L}}{\partial q_\alpha}\delta q_\alpha(t) - \frac{d}{dt}\left(\frac{\partial\mathcal{L}}{\partial\dot{q}_\alpha}\right)\delta q_\alpha(t)\right]dt = 0$

Constraints

$\sum_{\alpha=1}^{3N} a_{k\alpha}dq_\alpha + a_{kt}dt = 0, k = 1, \ldots, N_C$

Holonomic $a_{k\alpha} = \frac{\partial\sigma_k}{\partial q_\alpha} \qquad a_{kt} = \frac{\partial\sigma_k}{\partial t}$

Non-holonomic $\frac{1}{2}\sum_i m_i\dot{\vec{r}}_i^2 - C = 0 \Rightarrow \frac{1}{2}\sum_i m_i\dot{\vec{r}}_i d\dot{\vec{r}}_i - Cdt = 0$

$\Rightarrow a_{1i} = \frac{1}{2}m_i\dot{\vec{r}}_i \wedge a_{1t} = -C$

Lagrange multiplier $\frac{d}{dt}\left(\frac{\partial\mathcal{L}}{\partial\dot{q}_\alpha}\right) - \frac{\partial\mathcal{L}}{\partial q_\alpha} = \sum_{k=1}^{N_C}\lambda_k a_{k\alpha}$

$\dot{q}_\alpha = \frac{\partial\mathcal{H}}{\partial p_\alpha} \qquad \dot{p}_\alpha = -\frac{\partial\mathcal{H}}{\partial q_\alpha} - \sum_{k=1}^{N_C}\lambda_k a_{k\alpha} \qquad \sum_{\alpha=1}^{3N} a_{k\alpha}\frac{\partial\mathcal{H}}{\partial p_\alpha} = 0$

Simulation $m_i\ddot{\vec{r}}_i = \vec{F}_i + \sum_{k=1}^{N_C}\lambda_k\nabla_i\sigma_k \qquad \dot{\sigma}_k = \sum_{i=1}^N\nabla_i\sigma_k\cdot\dot{\vec{r}}_i = 0$

Velocity Verlet $\vec{r}_i(\Delta t) = \vec{r}_i(0) + \Delta t\vec{v}_i(0) + \frac{\Delta t^2}{2m_i}\vec{F}_i(0) + \frac{\Delta t^2}{2m_i}\sum_k\lambda_k\nabla_i\sigma_k(0)$

$\vec{r}_i(\Delta t) = \vec{r}_i + \frac{1}{m_i}\sum_k\tilde{\lambda}_k\nabla_i\sigma_k(0) \qquad \tilde{\lambda}_k = \frac{\Delta t^2}{2}\lambda_k$

$\sigma_l\left(\vec{r}_1^{(1)}, \ldots, \vec{r}_N^{(1)}\right) + \sum_{i=1}^N\sum_{k=1}^{N_C}\frac{1}{m_i}\nabla_i\sigma_k\left(\vec{r}_1^{(1)}, \ldots, \vec{r}_N^{(1)}\right)\cdot\nabla_i\sigma_k(\vec{r}_1(0), \cdots, \vec{r}_N(0))\delta\tilde{\lambda}_k \approx 0$

Direct translation

Liouville operator

Computable on $a : \frac{da}{dt} = \{a, \mathcal{H}\}$

$iL = \sum_\alpha\left[\frac{\partial\mathcal{H}}{\partial p_\alpha}\frac{\partial}{\partial q_\alpha} - \frac{\partial\mathcal{H}}{\partial q_\alpha}\frac{\partial}{\partial p_\alpha}\right] \Rightarrow iLa = \{a, \mathcal{H}\} \Rightarrow \frac{da}{dt} = iLa \Rightarrow a(x_t) = e^{iLt}a(x_0)$

Split $iL_1 = \sum_\alpha\frac{\partial\mathcal{H}}{\partial p_\alpha}\frac{\partial}{\partial q_\alpha} \qquad iL_2 = -\sum_\alpha\frac{\partial\mathcal{H}}{\partial q_\alpha}\frac{\partial}{\partial p_\alpha}$

$iL_1 iL_2\phi(x) \neq iL_2 iL_1\phi(x) \Rightarrow iL_1 iL_2 - iL_2 iL_1 \equiv [iL_1, iL_2] \neq 0$

Trotter theorem

$[iL_1, iL_2] \neq 0 \Rightarrow e^{iLt} \neq e^{iL_1t}e^{iL_2t}$

$e^{A+B} = \lim_{P\to\infty}\left[e^{\frac{B}{2P}}e^{\frac{A}{P}}e^{\frac{B}{2P}}\right]^P \qquad e^{iLt} = \lim_{P\to\infty}\left[e^{\frac{iL_2t}{2P}}e^{\frac{iL_1t}{P}}e^{\frac{iL_2t}{2P}}\right]^P$

$e^{iLt} \approx e^{\frac{iL_2\Delta t}{2}}e^{iL_1\Delta t}e^{\frac{iL_2\Delta t}{2}}$

Trotter algorithm

Exponential operator $e^{c\frac{\partial}{\partial x}}g(x) = g(x + c)$

$$\begin{pmatrix} x(\Delta t) \\ p(\Delta t) \end{pmatrix} = \begin{pmatrix} x(0) + \frac{\Delta t}{m}\left(p(0) + \frac{\Delta t}{2}F(x(0))\right) \\ p(0) + \frac{\Delta t}{2}F(x(0)) + \frac{\Delta t}{2}F\left(x(0) + \frac{\Delta t}{m}\left(p(0) + \frac{\Delta t}{2}F(x(0))\right)\right) \end{pmatrix}$$

$x(\Delta t) = x(0) + v(0)\Delta t + \frac{\Delta t^2}{2m}F(0) \qquad p(\Delta t) = v(0) + \frac{\Delta t}{2m}[F(0) + F(\Delta t)]$

RESPA

$iL = \frac{p}{m}\frac{\partial}{\partial x} + [F_{fast}(x) + F_{slow}(x)]\frac{\partial}{\partial p} = iL_{fast} + iL_{slow} \qquad \mathcal{H}_{ref} = \frac{p^2}{2m} + U_{fast}(x)$

$e^{iL\Delta t} = e^{iL_{slow}\frac{\Delta t}{2}}e^{iL_{fast}\Delta t}e^{iL_{slow}\frac{\Delta t}{2}}$

$e^{iL_{fast}\Delta t} = \left[e^{\frac{\delta t}{2}F_{fast}\frac{\partial}{\partial p}}e^{\delta t\frac{p}{m}\frac{\partial}{\partial x}}e^{\frac{\delta t}{2}F_{fast}\frac{\partial}{\partial p}}\right]^n \qquad \delta t = \frac{\Delta t}{n}$

Evaluation of energy and forces

Periodic boundary condition

Non bonded interaction $U_{nb}(\vec{r}_1, \ldots, \vec{r}_N) = \sum_{i<j\in nb}\left\{4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^6\right] + \frac{q_iq_j}{r_{ij}}\right\}$

Error function $erf(x) = \frac{2}{\sqrt{\pi}}\int_0^x e^{-t^2}dt \qquad \lim_{x\to\infty} erf(x) = 1 \qquad erf(0) = 0$

Complement error $erfc(x) = 1 - erf(x) = \frac{2}{\sqrt{\pi}}\int_x^\infty e^{-t^2}dt \qquad \lim_{x\to\infty} erf(x) = 0 \qquad erf(0) = 1$

$\frac{1}{r} = \overbrace{\frac{erfc(\alpha r)}{r}}^{\text{short-ranged}} + \overbrace{\frac{erf(\alpha r)}{r}}^{\text{long-ranged}} \qquad U_{nb} = U_{short} + U_{long} \qquad \vec{r}_{ij} = |\vec{r}_i - \vec{r}_j + \vec{S}| \qquad \vec{S} = \vec{m}L$

$U_{short}(\vec{r}_1, \ldots, \vec{r}_N) = \sum_{\vec{S}}\sum_{i>j\in nb}\left\{4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij,\vec{S}}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij,\vec{S}}}\right)^6\right] + \frac{q_iq_jerfc(\alpha r_{ij,\vec{S}})}{r_{ij,\vec{S}}}\right\}$

$U_{long}(\vec{r}_1, \ldots, \vec{r}_N) = \sum_{\vec{S}}\sum_{i>h\in nb}\frac{q_iq_jerf(\alpha r_{ij,\vec{S}})}{r_{ij,\vec{S}}}$

Short range forces

$\tilde{U}_{short} = U_{short}(\vec{r}_{ij})S(\vec{r}_{ij}) \qquad S(r) = \begin{cases} 1 & r < r_C - \lambda \\ 1 + \left(\frac{r - r_C + \lambda}{\lambda}\right)^2\left(2\frac{r - r_C + \lambda}{\lambda} - 3\right) & r_C - \lambda \neq r \leq r_C \\ 0 & r > r_C \end{cases}$

Evaluation of energy and forces (contd)

Long range forces

$C_{\vec{g}} = \frac{4\pi}{|\vec{g}|^2}e^{-\frac{|\vec{g}|^2}{4\alpha^2}} \qquad \frac{1}{V}\sum_{\vec{g}} C_{\vec{g}}e^{i\vec{g}\cdot\vec{r}} = \frac{1}{V}\sum_{i\neq j} q_iq_j\sum_{\vec{g}\in\mathcal{S}}\frac{4\pi}{|\vec{g}|^2}e^{-\frac{|\vec{g}|^2}{2\alpha^2}}e^{i\vec{g}\cdot(\vec{r}_i - \vec{r}_j)}$

$U_{long} = \frac{1}{V}\sum_{i,j} q_iq_j\sum_{\vec{g}\in\mathcal{S}}\frac{4\pi}{|\vec{g}|^2}e^{-\frac{|\vec{g}|^2}{4\alpha^2}}e^{i\vec{g}\cdot(\vec{r}_i - \vec{r}_j)} - \frac{1}{V}\sum_i q_i^2\sum_{\vec{g}\in\mathcal{S}}\frac{4\pi}{|\vec{g}|^2}e^{-\frac{|\vec{g}|^2}{4\alpha^2}}$

$U_{long} = \frac{1}{V}\sum_{\vec{g}\in\mathcal{S}}\frac{4\pi}{|\vec{g}|^2}e^{-\frac{|\vec{g}|^2}{4\alpha^2}}|S(\vec{g})|^2 - \frac{\alpha}{\sqrt{\pi}}\sum_i q_i^2$

Particle-particle particle-mesh Ewald

$\rho(\vec{r}) = \sum_i q_i\delta(\vec{r} - \vec{r}_i) \qquad \rho(\vec{g}) = \int d\vec{r}\rho(\vec{r})e^{i\vec{g}\cdot\vec{r}} = \sum_i q_ie^{i\vec{g}\cdot\vec{r}_i}$

$\nabla^2\phi(\vec{r}) = -\nabla\cdot\vec{E} = -4\pi\rho(\vec{r}) \qquad g^2\phi(\vec{g}) = -4\pi\rho(\vec{g}) = 4\pi S(\vec{g})$

Canonical ensemble

Thermodynamics

Helmholtz free energy $A(N, V, T) = E(N, V, T) - TS(N, V, T)$

$dA = SdT - PdV + \mu dN \qquad S = -\left(\frac{\partial A}{\partial T}\right)_{N,V} \qquad P = -\left(\frac{\partial A}{\partial V}\right)_{N,T} \qquad \mu = \left(\frac{\partial A}{\partial N}\right)_{V,T}$

Thermal contact

Microcanonical $\Omega(N, V, E) = M_N\int dx_1dx_2\delta(\mathcal{H}_1(x_1) + \mathcal{H}_2(x_2) - E)$

Distribution function $\ln f(x_1) = \ln\int dx_2\delta(\mathcal{H}_1(x_1) + \mathcal{H}_2(x_2) - E)$

$\ln f(x_1) \approx \ln\int dx_2\delta(\mathcal{H}_2(x_2) - E) - \frac{\partial}{\partial E}\ln\int dx_2\delta(\mathcal{H}_2(x_2) - E)\mathcal{H}_1(x_1)$

$Q(N, V, T) = \frac{1}{N!h^{3N}}\int dxe^{-\beta\mathcal{H}(x)} \qquad \beta = \frac{1}{kT}$

From micro to macro

$A = E - \beta\left(\frac{\partial A}{\partial\beta}\right)_{N,V}$

$E = \langle\mathcal{H}\rangle = \frac{1}{N!h^{3N}}\frac{\int dx\mathcal{H}(x)e^{-\beta\mathcal{H}(x)}}{\int dxe^{-\beta\mathcal{H}(x)}} = -\frac{1}{Q(N,V,\beta)}\frac{\partial Q(N,V,\beta)}{\partial\beta} = -\frac{\partial\ln Q(N,V,\beta)}{\partial\beta}$

$A + \frac{\partial\ln Q}{\partial\beta} + \beta\frac{\partial A}{\partial\beta} = 0 \Rightarrow \ln Q(N, V, \beta) = -\beta A(N, V, \beta)$

$A(N, V, T) = -kT\ln Q(N, V, T) \qquad C_N = \frac{1}{N!h^{3N}}$

Energy $E = \langle\mathcal{H}\rangle = \frac{1}{Q}\frac{\partial Q}{\partial\beta} = 0$

Temperature estimator $\mathcal{T}(x) + \frac{1}{3Nk}\sum_i\frac{\vec{p}_i^2}{m_i} \qquad T = \langle\mathcal{T}(x)\rangle = \frac{C_N\int dx\mathcal{T}(x)e^{-\beta\mathcal{H}(x)}}{C_N\int dxe^{-\beta\mathcal{H}(x)}}$

Energy fluctuation $\Delta E^2 = \frac{\partial^2\ln Q}{\partial\beta^2} = kT^2C_V \qquad \frac{\Delta E}{E} \sim \frac{1}{\sqrt{N}}$

Pressure estimator $\mathcal{P}(\vec{r}, \vec{p}) = \frac{1}{3V}\sum_i\left[\frac{\vec{p}_i^2}{m_i} + \vec{F}_i\cdot\vec{r}_i\right]$