Computational biophysics

Protein's geometry

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

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

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

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

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 $U_{AB} = \frac{q_Aq_B}{\epsilon_{AB}r_{AB}}$

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

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

Classical mechanics

Newton's laws

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

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

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

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: $U=\frac{332q_iq_j}{\epsilon r_{ij}}$

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

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

Lagrangian formulation

$\vec{F}_i(\vec{r}_1,\dots,\vec{r}_N)=-\Delta_iU(\vec{r}_1,\dots,\vec{r}_N)$

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

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

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

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

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

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

Generalized coordinates

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

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

Classical mechanics (contd)

Legendre transforms

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

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

$\tilde f(s_1,\dots,s_n)=f(x_1(s_1,\dots,s_n),\dots x_n(s_1,\dots,s_n))-\sum_i s_ix_i(s_1,\dots,s_n)$

Hamiltonian formulation

$\mathcal{H}(\vec r_1,\dots,\vec r_N,\vec p_1,\dots,\vec p_N)=-\tilde{\mathcal{L}}(\vec r_1,\dots,\vec r_N,\vec p_1,\dots,\vec p_N)$

$\mathcal{H}(\vec r_1,\dots,\vec r_N,\vec p_1,\dots,\vec p_N)=\sum_{i=1}^N\frac{\vec p_i^2}{2m_i}+U(\vec r_1,\dots,\vec r_N)$

$\mathcal{H}(q_1,\dots,q_{3N},p_1,\dots,p_{3N})=\frac12\sum_\alpha\sum_\beta p_\alpha G^{-1}_{\alpha\beta}p_\beta+U(q_1,\dots,q_{3N})$

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

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 $M=J^TMJ$ $J_{kl}=\frac{\partial x_k(t)}{\partial x_l(0)}$

Theoretical foundations of statistical mechanics

Thermodynamics

Equilibrium $g(N,P,V,T)=0$ First law $\Delta E=\Delta Q+\Delta W$

State function $f(n,P,V,T)$ Entropy $\Delta S=\int_1^2\frac{dQ_{rev}}{T}$

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

Heat $dQ_{rev}=CdT$

The ensemble

Average $A=\frac1Z\sum_{\lambda=1}^N a(x_\lambda)\equiv\langle a\rangle$

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

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

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

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

$Z=\int dx\mathcal F(\mathcal H(x))\Rightarrow f(x)=\frac1Z\mathcal F(\mathcal H(x))$

Microcanonical ensemble

State and distribution function

State function $dS=\frac1TdE+\frac PTdV-\frac\mu TdN$

$\left(\frac{\partial S}{\partial E}\right)_{V,N}=\frac1T$ $\left(\frac{\partial S}{\partial V}\right)_{N,E}=\frac PT$ $\left(\frac{\partial S}{\partial N}\right)_{V,N}=\frac\mu T$

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 $=M_N\int dx\delta(\mathcal H(x)-E)$

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

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

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

Virial theorem

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

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

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

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

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

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

Introduction to molecular dynamics (contd)

Action integral

$Q\equiv\{q_1,\dots,q_{3N}\}$ $\dot Q\equiv\{\dot q_1,\dots,\dot q_{3N}\}$

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

$\delta Q(t_1)=\delta Q(t_2)=0$ $\delta\dot Q(t_1)=\delta\dot Q(t_2)=0$

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

Constraints

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

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

Non-holonomic $\frac12\sum_i m_i\dot{\vec r}_i^2-C=0\Rightarrow\frac12\sum_i m_i\dot{\vec r}_id\vec r_i-Cdt=0$

$\Rightarrow a_{1i}=\frac12 m_i\dot{\vec r}_i\wedge a_{1t}=-C$

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

$\dot q_\alpha=\frac{\partial\mathcal H}{\partial p_\alpha}$ $\dot p_\alpha=-\frac{\partial\mathcal H}{\partial q_\alpha}-\sum_{k=1}^{N_C}\lambda_ka_{k\alpha}$ $\sum_{\alpha=1}^{3N}a_{k\alpha}\frac{\partial\mathcal H}{\partial p_\alpha}=0$

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

Velocity Verlet $\vec r_i(\Delta t)=\vec r_i(0)+\Delta t\vec v_i(0)+\frac{\Delta t^2}{2m_i}\vec F_i(0)+\frac{\Delta t^2}{2m_i}\sum_k\lambda_k\nabla_i\sigma_k(0)$

$\vec r_i(\Delta t)=\vec r_i'+\frac{1}{m_i}\sum_k\tilde\lambda_k\nabla_i\sigma_k(0)$ $\tilde\lambda_k=\frac{\Delta t^2}{2}\lambda_k$

$\sigma_l\left(\vec r_1^{(1)},\dots,\vec r_N^{(1)}\right)+\sum_{i=1}^N\sum_{k=1}^{N_C}\frac{1}{m_i}\nabla_i\sigma_k\left(\vec r_1^{(1)},\dots,\vec r_N^{(1)}\right)\cdot\nabla_i\sigma_k(\vec r_1(0),\cdots,\vec r_N(0))\delta\tilde\lambda_k\approx0$

Direct translation

Liouville operator

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

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

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

$iL_1iL_2\phi(x)\neq iL_2iL_1\phi(x)\Rightarrow iL_1iL_2-iL_2iL_1\equiv[iL_1,iL_2]\neq0$

Trotter theorem

$[iL_1,iL_2]\neq0\Rightarrow e^{iLt}\neq e^{iL_1t}e^{iL_2t}$

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

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

Trotter algorithm

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

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

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

RESPA

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

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

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

Evaluation of energy and forces

Periodic boundary condition

Non bonded interaction $U_{nb}(\vec r_1,\dots,\vec r_N)=\sum_{i<j\in nb}\left\{4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12}-\left(\frac{\sigma_{ij}}{r_{ij}}\right)^6\right]+\frac{q_iq_j}{r_{ij}}\right\}$

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

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

$\frac1r=\overbrace{\frac{erfc(\alpha r)}{r}}^{\text{short-ranged}}+\overbrace{\frac{erf(\alpha r)}{r}}^{\text{long-ranged}}$ $U_{nb}=U_{short}+U_{long}$ $\vec r_{ij}=|\vec r_i-\vec r_j+\vec S|$ $\vec S=\vec mL$

$U_{short}(\vec r_1,\dots,\vec r_N)=\sum_{\vec S}\sum_{i>j\in nb}\left\{4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij,\vec S}}\right)^{12}-\left(\frac{\sigma_{ij}}{r_{ij,\vec S}}\right)^6\right]+\frac{q_iq_jerfc(\alpha r_{ij,\vec S})}{r_{ij,\vec S}}\right\}$

$U_{long}(\vec r_1,\dots,\vec r_N)=\sum_{\vec S}\sum_{i>h\in nb}\frac{q_iq_jerf(\alpha r_{ij,\vec S})}{r_{ij,\vec S}}$

Short range forces

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

Evaluation of energy and forces (contd)

Long range forces

$C_{\vec g}=\frac{4\pi}{|\vec g|^2}e^{-\frac{|\vec g|^2}{4\alpha^2}}$ $\frac1V\sum_{\vec g}C_{\vec g}e^{i\vec g\cdot\vec r}=\frac1V\sum_{i\neq j}q_iq_j\sum_{\vec g\in\mathcal S}\frac{4\pi}{|\vec g|^2}e^{-\frac{|\vec g|^2}{2\alpha^2}}e^{i\vec g\cdot(\vec r_i-\vec r_j)}$

$U_{long}=\frac1V\sum_{i,j}q_iq_j\sum_{\vec g\in\mathcal S}\frac{4\pi}{|\vec g|^2}e^{-\frac{|\vec g|^2}{4\alpha^2}}e^{i\vec g\cdot(\vec r_i-\vec r_j)}-\frac1V\sum_iq_i^2\sum_{\vec g\in\mathcal S}\frac{4\pi}{|\vec g|^2}e^{-\frac{|\vec g|^2}{4\alpha^2}}$

$U_{long}=\frac1V\sum_{\vec g\in\mathcal S}\frac{4\pi}{|\vec g|^2}e^{-\frac{|\vec g|^2}{4\alpha^2}}|S(\vec g)|^2-\frac{\alpha}{\sqrt\pi}\sum_iq_i^2$

Particle-particle particle-mesh Ewald

$\rho(\vec r)=\sum_iq_i\delta(\vec r-\vec r_i)$ $\rho(\vec g)=\int d\vec r\rho(\vec r)e^{i\vec g\cdot\vec r}=\sum_iq_ie^{i\vec g\cdot\vec r_i}$

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

Canonical ensemble

Thermodynamics

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

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

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 $\ln f(x_1)=\ln\int dx_2\delta(\mathcal H_1(x_1)+\mathcal H_2(x_2)-E)$

$\ln f(x_1)\approx\ln\int dx_2\delta(\mathcal H_2(x_2)-E)-\frac{\partial}{\partial E}\ln\int dx_2\delta(\mathcal H_2(x_2)-E)\mathcal H_1(x_1)$

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

From micro to macro

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

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

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

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

Energy $E=\langle\mathcal H\rangle=\frac1Q\frac{\partial Q}{\partial\beta}=0$

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

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

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

Thermostats

Velocity rescaling

$\bar K=\frac{N_j}{2\beta}$ $K=\frac12\sum_im_i\vec v_i^2$ $\vec v_i\to\frac{\vec v_i}{\alpha}$ $\alpha=\sqrt{\frac{\bar K}{K}}$

$\bar K=\frac12\sum_im_i\frac{\vec v_i^2}{\alpha^2}=\frac{\bar K}{2K}\sum_im_i\vec v_i^2$

Andersen-Heyes Thermostat

$P(p)=\left(\frac{\beta}{2\pi m}\right)^{\frac32e^{-\beta\frac{p^2}{2m}}}$

$P(K_t)dK_t\propto K_t^{\frac{N_f}{2}-1}e^{-\beta K_t}dK_t$

$K_t=\frac12\sum_im_i\frac{\vec v_i^2}{\alpha^2}=\frac{K_t}{2K}\sum_im_i\vec v_i^2$

Langevin Thermostat

$\dot{\vec r}_i(t)=\beta D\vec F_i(\vec r_1(t),\dots,\vec r_N(t))+\eta_i(t)$ $\frac{\partial}{\partial t}P(\vec x,t)=D\sum_{i=1}^N\nabla_i\cdot[\nabla_i+\beta\nabla\mathcal H(\vec x)]$

$P(\vec x)=Ce^{-\beta\mathcal H(\vec x)}$ $\langle\eta_i(t)\eta_j(t)\rangle=6D\delta_{ij}\frac{\delta_{kl}}{\Delta t}$ $\sigma^2=\frac{6D}{\Delta t}$

$\xi_i(t_k)=\sqrt{\frac{\Delta t}{6D}}\eta_i(t_k)$ $\langle\xi_i(t_k)\rangle=0$ $\langle\xi_i(t_k)\xi_j(t_l)\rangle=\delta_{ij}\delta_{kl}$

$\vec r_i(t+\Delta t)=\vec r_i(t)+\Delta t\frac{\vec F_i(\vec r_1(t),\dots,\vec r_N(t))}{m_i\gamma}+\sqrt{\frac{6kT\Delta t}{m_i\gamma}}\xi_i(t)$

j

Bussi velocity Verlet

$dK=\left(D(K)\frac{\partial\log P(K)}{\partial K}+\frac{\partial D(K)}{\partial K}\right)dt+\sqrt{2D(K)}dW$ $P(K_t)dK_t\propto K_t^{\frac{N_f}{2}1}e^{\beta K_t}dK$

$dK=\left(\frac{N_fD(K)}{2K\bar K}(K-\bar K)-\frac{D(K)}{K}+\frac{\partial D(K)}{\partial K}\right)dt+\sqrt{2D(K)}dW$ $D(K)=\frac{2K\bar K}{N_f\tau}$

$dK=(K-\bar K)\frac{dt}{\tau}+\sqrt{\frac{2K\bar K}{N_f}}\frac{dW}{\sqrt\tau}$

Berendsen's thermostat $dK=(K-\bar K)\frac{dt}{\tau}$

$\alpha^2=e^{-\frac{\Delta t}{\tau}}+\frac{\bar K}{N_fK}\left(1-e^{-\frac{\Delta t}{\tau}}\right)\sum_{i=1}^{N_f}R_i^2+2e^{-\frac{\Delta t}{2\tau}}\sqrt{\frac{\bar K}{N_fK}\left(1-e^{-\frac{\Delta t}{\tau}}R_1\right)}$

Nosè Hamiltonian

$\mathcal H_N=\sum_i\frac{\vec p_i^2}{2m_is^2}+U(\vec r_1,\dots,\vec r_n)+\frac{p_s^2}{2Q}+gkT\log s$

$\Omega=\int d^N\vec rd^N\vec pdsdp_ss^{dN}\delta\left(\mathcal H+\frac{p_s^2}{2Q}+gkT\log s-E\right)$

$\Omega=\frac{1}{dkT}\int d^N\vec rd^N\vec pdp_se^{\frac{dN+1}{gkT}\left(E-\mathcal H-\frac{p_s^2}{2Q}\right)}$

$g=dN+1\Rightarrow\Omega=\frac{e^{\frac{e}{kT}}\sqrt{2\pi QkT}}{(dN+1)kT}\int d^N\vec rd^N\vec pe^{-\frac{\mathcal H}{kT}}$

$\dot{\vec r}_i=\frac{\vec p_i}{m_i}s^2$ $\dot{\vec p}_i=\vec F_i$ $\dot s=\frac{p_s}{Q}$ $\dot p_s=\frac1s\left[\sum_i\frac{\vec p_i^2}{m_is^2}-gkT\right]$

Thermostats (contd)

Nosè-Hoover equations

$\vec{p}'_i = \frac{\vec{p}_i}{s}$ $\quad \vec{p}'_s = \frac{p_s}{s}$ $\quad dt' = \frac{dt}{s}$ $\quad \frac{d\vec{r}_i}{dt'} = \frac{\vec{p}'_i}{m_i}$ $\quad \frac{d\vec{p}'_i}{dt'} = \vec{F}_i - \frac{s p'_s}{Q}\vec{p}'_i$

$\frac{ds}{dt'} = \frac{s^2 p'_s}{Q}$ $\quad \frac{dp'_s}{dt'} = \frac{1}{2}\left[\sum_i \frac{(\vec{p}'_i)^2}{m_i} - gkT\right]^2 - \frac{s(p'_s)^2}{Q}$ $\quad \frac{1}{2}\frac{ds}{dt'} = \frac{d\eta}{dt'}$ $\quad p_s = p_\eta = s p'_s$

$\dot{\vec{r}}_i = \frac{\vec{p}_i}{m_i}$ $\quad \dot{\vec{p}}_i = \vec{F}_i - \frac{P_\eta}{Q}\vec{p}_i$ $\quad \dot{\eta} = \frac{p_\eta}{Q}$ $\quad \dot{p}_\eta = \sum_i \frac{\vec{p}_i^2}{m_i} - dNkT$

Non Hamiltonian statistical mechanics

$\dot{x} = \xi(x,t)$ $\quad \nabla\cdot\dot{x} = \nabla\cdot\xi(x,t) = \kappa(x,t) \neq 0$

$J(x_t;x_0) = e^{\int_0^t ds\kappa(x_s,s)}$ $\quad \kappa(x_t,t) = \frac{dw(x_t,t)}{dt} \Rightarrow J(x_t;x_0) = e^{w(x_t,t)-w(x_0,0)}$ $\quad e^{-w(x_t,t)}dx_t = e^{-w(x_0,0)}dx_0$

$J(x_t;x_0) = \frac{\sqrt{g(x_0,0)}}{\sqrt{g(x_t,t)}}$ $\quad \sqrt{g(x_t,t)} = e^{-w(x_t,t)}$

$\frac{\partial}{\partial t}\left[f(x,t)\sqrt{g(x,t)}\right] + \nabla\cdot\left[\dot{x}\sqrt{g(x,t)}f(x,t)\right] = 0$ $\quad f(x_t,t)\sqrt{g(x_t,t)}dx_t = f(x_0)\sqrt{g(x_0)}dx_0$ $\quad \xi(x)\cdot\nabla f(x) = 0$

$\Lambda_k(x_t) - C_k = 0$ $\quad \frac{d\Lambda_k(x_t)}{dt} = 0 \Rightarrow f(x) = \prod_{k=1}^{N_C}\delta(\Lambda_k(x_t) - C_k)$

Microcanonical $\mathcal{E} = \int dx\sqrt{g(x)}f(x) = \int dx\sqrt{g(x)}\prod_{k=1}^{N_C}\delta(\Lambda_k(x_t) - C_k)$

Nosè=Hoover: $\mathcal{H}'(\vec{r},\eta,\vec{p},p_\eta) = \mathcal{H}(\vec{r},\vec{P}) + \frac{p_\eta^2}{2Q} + dNkT\eta$ $\quad \frac{d\mathcal{H}'}{dt} = 0$

$\kappa = -Nd\dot{\eta} \Rightarrow \sqrt{g} = e^{dN\eta}$

Partition function $\mathcal{E}_T(N,V,C_1) = \frac{e^{\beta C_1}\sqrt{2\pi QkT}}{dNkT}\int d^N\vec{p}\int_{\mathcal{D}(V)} d^N\vec{r}e^{-\beta\mathcal{H}(\vec{r},\vec{p})}$

$\vec{P} = \sum_{i=1}^N \vec{p}_1$ $\quad \vec{K} = \vec{P}e^\eta \Rightarrow \frac{d\vec{K}}{dt} = 0$

Nosè-Hoover chains

$\dot{\vec{r}}_i = \frac{\vec{p}_i}{m_i}$ $\quad \dot{\vec{p}}_i = \vec{F}_i - \frac{p_{\eta_1}}{Q_1}\vec{p}_i$ $\quad \dot{\eta}_j = \frac{p_{\eta_j}}{Q_j}$ $\quad j = 1,\ldots,M$

$\dot{p}_{\eta_1} = \left[\sum_i \frac{\vec{p}_i^2}{m_i} - dNkT\right] - \frac{p_{\eta_2}}{Q_2}p_{\eta_1}$ $\quad \dot{p}_{\eta_j} = \left[\sum_i \frac{\vec{p}_{\eta_{j-1}}^2}{Q_{j-1}} - kT\right] - \frac{p_{\eta_{j+1}}}{Q_{j+1}}p_{\eta_j}$ $\quad j = 2,\ldots,M-1$

$\dot{p}_{\eta_M} = \frac{p_{\eta_{M-1}}^2}{Q_{M-1}} - kT$

$\mathcal{H}'(\vec{r},\eta,\vec{p},p_\eta) = \mathcal{H}(\vec{r},\vec{p}) + \sum_{j=1}^M \frac{p_{\eta_j}^2}{2Q_j} + dNkT\eta_1 + kT\sum_{j=2}^M \eta_j$

$\kappa = -dN\dot{\eta}_1 - \dot{\eta}_c$ $\quad \eta_c = \sum_{j=2}^M \eta_j$ $\quad \sqrt{g} = e^{dN\eta_1 + \eta_c}$

Partition function $\mathcal{E}_T(N,V,C_1) = \mathcal{M}\int d^N\vec{p}\int_{\mathcal{D}(V)} d^N\vec{r}e^{-\beta\mathcal{H}(\vec{r},\vec{p})}$

Isobaric ensemble

Legendre transforms

Enthalpy $dH = TdS + \mu dN + VdP$ $\quad T = \left(\frac{\partial H}{\partial S}\right)_{N,P}$ $\quad \langle V\rangle = \left(\frac{\partial H}{\partial P}\right)_{N,S}$ $\quad \mu = \left(\frac{\partial H}{\partial N}\right)_{P,S}$

Gibbs $dG = \mu dN + VdP - SdT$ $\quad S = -\left(\frac{\partial G}{\partial T}\right)_{N,P}$ $\quad \langle V\rangle = -\left(\frac{\partial G}{\partial P}\right)_{N,T}$ $\quad \mu = -\left(\frac{\partial G}{\partial N}\right)_{P,T}$

Isoenthalpic-isobaric ensemble

$H = \mathcal{H}(v) + PV$ $\quad f(x) = F(\mathcal{H}(x)) = \mathcal{M}\delta(\mathcal{H}(x) + PV - H)$

$\Gamma(N,P,H) = \mathcal{M}\int_0^\infty dV\int d^N\vec{p}\int_{\mathcal{D}(V)} d^N\vec{r}\delta(\mathcal{H}(\vec{r}m\vec{p}) + PV - H)$

$S(N,P,H) = k\ln\Gamma(N,P,H)$ $\quad \frac{1}{T} = \left(\frac{\partial S}{\partial H}\right)_{N,P}$ $\quad \frac{\langle V\rangle}{T} = -\left(\frac{\partial S}{\partial P}\right)_{N,H}$ $\quad \frac{\mu}{T} = -\left(\frac{\partial S}{\partial N}\right)_{P,H}$

Isothermal-isobaric ensemble

$Q(N,V,T) \propto Q(N_1,V_1,T)Q(N_2,V_2,T)$

$f(x_1) = I_{N_1}e^{\beta\mu N_1}e^{-\beta PV_1}C_{N_1}e^{-\beta\mathcal{H}_1(x_1)}$ $\quad I_{N_1} = \frac{1}{V_0 N_1! h^{3N_1}}$

$\Delta(N,P,T) = \frac{1}{V_0}\int_0^\infty dVe^{-\beta PV}Q(N,V,T)$

$G(N,P,\beta) = -\frac{\partial\ln\Delta(N,P,\beta)}{\partial\beta} - \beta\frac{\partial G}{\partial\beta}$

Virial theorems

Pressure $\langle P^{(int)}\rangle = \frac{P}{\Delta(N,P,T)}\int_0^\infty dVe^{-\beta PV}Q(N,V,T) = P$ Work $\langle P^{(int)}V\rangle + kT = P\langle V\rangle$

Andersen's Hamiltonian

$\mathcal{H}_A = \sum_{i=1}^N \frac{V^{-\frac{2}{3}}\pi_i^2}{2m_i} + U(V^{\frac{1}{3}}\vec{s}_1,\ldots,V^{\frac{1}{3}}\vec{s}_N) + \frac{p_V^2}{2W} + PV$ $\quad W = (3N+1)kT\tau_b^2$

$\dot{\vec{s}}_i = \frac{p_i}{m_i} + \frac{\dot{V}}{3V}r_i$ $\quad \dot{\pi}_i = -\frac{\partial U}{\partial r_i} - \frac{\dot{V}}{3V}p_i$ $\quad \dot{V} = \frac{p_V}{W}$ $\quad \dot{p}_V = \frac{1}{3V}\sum_{i=1}^N\left[\frac{p_i^2}{m_i} - \frac{\partial U}{\partial r_i}r_i\right] - P$

$\dot{\vec{r}}_i = \frac{\vec{p}}{m_i} + \frac{\dot{V}}{3V}\vec{r}_i$ $\quad \dot{\vec{p}}_i = -\frac{\partial U}{\partial\vec{r}_i} - \frac{\dot{V}}{3V}\vec{p}_i$ $\quad \dot{V} = \frac{p_V}{W}$ $\quad \dot{p}_V = \frac{1}{3V}\sum_{i=1}^N\left[\frac{\vec{p}_i^2}{m_i} - \frac{\partial U}{\partial\vec{r}_i}\cdot\vec{r}_i\right] - P$

$\left\langle\frac{p_V^2}{2W}\right\rangle = k\frac{T}{2} \Rightarrow \mathcal{H}(\vec{r},\vec{p}) + PV$ is conserved

MTK algorithm

$\epsilon = \frac{1}{3}\ln\frac{V}{V_0} \Rightarrow \dot{\epsilon} = \frac{\dot{V}}{3V} = \frac{p_\epsilon}{W}$

$\dot{\vec{r}}_i = \frac{\vec{p}_i}{m_i} + \frac{p_\epsilon}{W}\vec{r}_i$ $\quad \dot{\vec{p}}_i = -\frac{\partial U}{\partial\vec{r}_i} - \frac{p_\epsilon}{W}\vec{p}_i$ $\quad \dot{V} = \frac{dVp_\epsilon}{W}$ $\quad \dot{p}_\epsilon = dV(\mathcal{P}^{(int)} - P)$

$\kappa = \frac{\dot{V}}{V}$ $\quad \dot{\vec{p}}_i = -\frac{\partial U}{\partial\vec{r}_i} - \left(1 + \frac{d}{N_F}\right)\frac{p_\epsilon}{W}\vec{p}_i$ $\quad \dot{p}_\epsilon = dV(\mathcal{P}^{(int)} - P) + \frac{d}{N_f}\sum_{i=1}^N \frac{\vec{p}_i^2}{m_i}$

Langevin piston $\dot{\vec{r}}_i = \frac{\vec{p}_i}{m_i} + \frac{\dot{V}}{3V}\vec{r}_i$ $\quad \dot{\vec{p}}_i = -\frac{\partial U}{\partial\vec{r}_i} - \frac{\dot{V}}{3V}\vec{p}_i$ $\quad \dot{V} = \frac{p_V}{W}$

$\dot{p}_V = \frac{1}{3V}\sum_{i=1}^N\left[\frac{\vec{p}_i^2}{m_i} - \frac{\partial U}{\partial\vec{r}_i}\cdot\vec{r}_i\right] - P - \gamma\dot{V} + R(t)$ $\quad \langle R(0)R(t)\rangle = \frac{2\gamma kT}{W}\delta(t)$