Mechanical quantities

notation here:
$U = U(r^N)$ = potential energy
$E = E(T, V)$ = internal energy
f = # of degrees of freedom

- Temperature (NVE MD):

$$T_{\text{kin}} = \frac{E_{\text{kin}}}{f k_{\text{B}}/2}$$

- Internal energy:

res = residual
see next slide

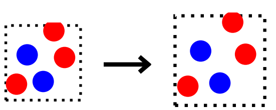
$$E = \langle E_{\text{kin}} + U \rangle \overset{NVT}{=} \frac{f}{2} k_{\text{B}} T + \langle U \rangle \equiv E_{\text{id}} + E_{\text{res}}$$

- Pressure

$\beta = 1/k_{\text{B}}T$

$$P = \frac{N}{V} k_{\text{B}} T - \left\langle \left(\frac{\partial U(V^{1/3} \vec{\xi}^N)}{\partial V} \right)_{\vec{\xi}^N} \right\rangle \equiv P_{\text{id}} + P_{\text{res}}$$

– dimensionless (scaled) coordinates $\vec{\xi}_i$: $\vec{r}_i = V^{1/3} \vec{\xi}_i$



– red derivative is calculated at const. $\vec{\xi}^N$, whole config. uniformly shrank/swelled
– P_{id} = kinetic contribution
– P_{res} = cohesion contribution

Pressure: formal derivation

$$\langle X\rangle = \frac{1}{Q_N}\int_{V^N} \exp[-\beta U(\vec{r}^N)]X(\vec{r}^N)\mathrm{d}\vec{r}^N$$

$$P = -\left(\frac{\partial F}{\partial V}\right)_T, \quad F = -k_\mathrm{B}T\ln\frac{Q_N}{N!\Lambda^{3N}}$$

$$Q_N = \int_{V^N}\exp[-\beta U(\vec{r}^N)]\mathrm{d}\vec{r}^N \overset{\vec{r}_i = V^{1/3}\vec{\xi}_i}{=} \int_{1^{3N}}\exp[-\beta U(V^{1/3}\vec{\xi}^N)]V^N\mathrm{d}\vec{\xi}^N$$

$$\begin{aligned}
P &= -\left(\frac{\partial F}{\partial V}\right)_T = k_\mathrm{B}T\left(\frac{\partial\ln Q_N}{\partial V}\right)_{\vec{\xi}^N} = \frac{k_\mathrm{B}T}{Q_N}\left(\frac{\partial Q_N}{\partial V}\right)_{\vec{\xi}^N}\\
&= \frac{k_\mathrm{B}T}{Q_N}\int_{1^{3N}}\exp[-\beta U(V^{1/3}\vec{\xi}^N)]NV^{N-1}\mathrm{d}\vec{\xi}^N\\
&\quad + \frac{k_\mathrm{B}T}{Q_N}\int_{1^{3N}}\exp[-\beta U(V^{1/3}\vec{\xi}^N)](-\beta)\left(\frac{\partial U(V^{1/3}\vec{\xi}^N)}{\partial V}\right)_{\vec{\xi}^N}V^N\mathrm{d}\vec{\xi}^N\\
&= \frac{N}{V}k_\mathrm{B}T - \left\langle\left(\frac{\partial U(V^{1/3}\vec{\xi}^N)}{\partial V}\right)_{\vec{\xi}^N}\right\rangle
\end{aligned}$$

Residual quantities

= with respect to the standard state of ideal gas at the same temperature, volume, and composition as the given system. Usefull in the canonical (NVT) ensemble.

sometimes called “excess”

For the Helmholtz energy:

ideal gas: $Q_N = V^N$

$$F = -k_\mathrm{B}T \ln Z_N = -k_\mathrm{B}T \ln \frac{Q_N}{N!\Lambda^{3N}} = -k_\mathrm{B}T \ln \frac{V^N}{N!\Lambda^{3N}} - k_\mathrm{B}T \ln \frac{Q_N}{V^N} \equiv F_\mathrm{id} + F_\mathrm{res}$$

Refresh:

de Broglie thermal wavelength:

$$\Lambda = \frac{h}{\sqrt{2\pi m k_\mathrm{B}T}}$$

chemical potential of ideal gas:

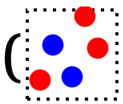
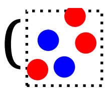
$$\mu_\mathrm{id} = \left(\frac{\partial F_\mathrm{id}}{\partial N}\right)_{T,V} = k_\mathrm{B}T \ln \frac{N\Lambda^3}{V}$$

Pressure – virtual volume change method

$$P = \frac{N}{V}k_\mathrm{B}T - \left\langle \left(\frac{\partial U(V^{1/3}\vec{\xi}^N)}{\partial V} \right)_{\vec{\xi}^N} \right\rangle$$

Numerical derivative (for a selected series of configurations)

$$\frac{\partial U}{\partial V} = \frac{U(V+\Delta V)-U(V)}{\Delta V} + \mathcal{O}(\Delta V) \equiv$$

$U($  $) - U($  $)$ divided by ΔV, $+\,\mathcal{O}(\Delta V)$

$$\frac{\partial U}{\partial V} = \frac{U(V+\Delta V)-U(V-\Delta V)}{2\Delta V} + \mathcal{O}(\Delta V^2)$$

Implementation: $U(V+\Delta V)$ means that the whole configuration (all distances) is swelled by the same ratio; for molecules w.r.t. a ref. point (then, N = # of molecules):

$$\left(\frac{V+\Delta V}{V}\right)^{1/3}.$$

The scaled configuration is not included in the trajectory.

For models with a hard core such that swelling the box cannot cause an overlap, shrinking can be used: $P = Nk_\mathrm{B}T/V + \frac{k_\mathrm{B}T}{\Delta V}\langle \mathrm{e}^{-[U(V-\Delta V)-U(V)]/k_\mathrm{B}T}\rangle + \mathcal{O}(\Delta V)$

Pressure – from the virial of force

The derivative expanded:

$$\frac{\partial U(V^{1/3}\vec{\xi}^N)}{\partial V} = \sum_{i=1}^{N} \frac{1}{3} V^{-2/3} \vec{\xi}_i \cdot \underbrace{\frac{\partial U}{\partial \vec{r}_i}}_{-\vec{f}_i} = \frac{1}{3V} \sum_{i=1}^{N} \vec{r}_i \cdot \frac{\partial U}{\partial \vec{r}_i}$$

The result is

$$PV = N k_\mathrm{B} T + \frac{1}{3}\langle W_f \rangle \qquad W_f = -\sum_{i=1}^{N} \vec{r}_i \cdot \frac{\partial U}{\partial \vec{r}_i} = \sum_{i=1}^{N} \vec{r}_i \cdot \vec{f}_i \quad \text{(virial of force)}$$

... cannot be directly applied in the periodic boundary conditions.

- Pair additivity in the periodic boundary conditions ⇒

$$P = \frac{N}{V} k_\mathrm{B} T - \frac{1}{3V} \sum_{i<j} \langle r_{ij} u'(r_{ij}) \rangle \equiv P_\mathrm{id} + P_\mathrm{res}$$

Entropic quantities

We need to know a partition function: $F \to G, S, \mu \ldots$

- thermodynamic integration:
  over a real variable (T, V, P) or coupling parameter
- Widom particle insertion method
- non-Boltzmann sampling:
  gradual insertion, alchemical transmutation;
  umbrella sampling
  multiple histogram reweighting
- reversible work calculated by the integration of force
- local density method

Thermodynamic integration

Remember physical chemistry: $\mathrm{d}F = -S\mathrm{d}T - p\mathrm{d}V$, $\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p$

Canonical ensemble: (E = internal energy)

$$\left(\frac{\partial F}{\partial V}\right)_T = -P, \quad \left(\frac{\partial(\beta F)}{\partial \beta}\right)_V = E, \quad \text{or} \quad \left(\frac{\partial(\beta F_{\mathrm{res}})}{\partial \beta}\right)_V = \langle U \rangle$$

- Numerically integrated – P, E must be determined in many points
- Start from a known state (ideal gas, hard spheres, Lennard-Jones, Einstein cryst.)

Proof # 1 of $\frac{\partial(\beta F)}{\partial \beta} = E$:

$$\frac{\partial(\beta F)}{\partial \beta} = \frac{\partial(F/T)}{\partial(1/T)} = \frac{\partial(F/T)}{\partial T} / \frac{\partial(1/T)}{\partial T} = \frac{-ST - F}{T^2} / \left(\frac{-1}{T^2}\right) = ST + F = E$$

Proof # 2 of $\frac{\partial(\beta F)}{\partial \beta} = E$:

$$\frac{\partial(\beta F)}{\partial \beta} = \frac{-\partial \ln Z}{\partial \beta} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -\frac{\frac{\partial \sum_\psi \mathrm{e}^{-\beta \mathcal{E}(\psi)}}{\partial \beta}}{\sum_\psi \mathrm{e}^{-\beta \mathcal{E}(\psi)}} = -\frac{\sum_\psi \left[-\mathcal{E}(\psi)\mathrm{e}^{-\beta \mathcal{E}(\psi)}\right]}{\sum_\psi \mathrm{e}^{-\beta \mathcal{E}(\psi)}} = \langle \mathcal{E} \rangle = E$$

Integration over a coupling parameter

Let us consider any dependence $(\beta U)(\lambda)$, e.g.:

$$(\beta U)(\lambda) = \begin{cases} \beta[U_0 + \lambda(U_1 - U_0)] & \lambda = \text{coupling parameter} \\ \lambda U & \lambda \equiv \beta\text{: see previous slide} \end{cases}$$

then

$$\frac{\partial \beta F_{\text{res}}}{\partial \lambda} = -\frac{\partial \ln Q}{\partial \lambda} = -\frac{1}{Q}\int \frac{\partial e^{-\beta U}}{\partial \lambda} d\mathbf{r}^N = \frac{1}{Q}\int \frac{\partial(\beta U)(\lambda)}{\partial \lambda} e^{-\beta U(\lambda)} d\mathbf{r}^N = \left\langle \frac{\partial(\beta U)(\lambda)}{\partial \lambda} \right\rangle_\lambda$$

$$(\beta F_{\text{res}})(\lambda_1) = (\beta F_{\text{res}})(\lambda_0) + \int_{\lambda_0}^{\lambda_1} \left\langle \frac{\partial(\beta U)(\lambda)}{\partial \lambda} \right\rangle_\lambda d\lambda$$

where $\langle\cdot\rangle_\lambda$ = mean value in the ensemble (simulation) with potential $U(\lambda)$

Example 1: for $\lambda = \beta$ we get as before:

$$\beta_1 F_{\text{res}}(\beta_1) - \beta_0 F_{\text{res}}(\beta_0) = \int_{\beta_0}^{\beta_1} \langle U \rangle d\beta$$

Example 2: integration from an Einstein crystal to a real crystal.

NB: Einstein crystal = independent harmonic oscillators at lattice sites

Non-Boltzmann sampling

We want $(\beta U)_1$, but we simulate $(\beta U)_0$ (can change β/U/both)

$$\Delta(\beta U) = (\beta U)_1 - (\beta U)_0$$

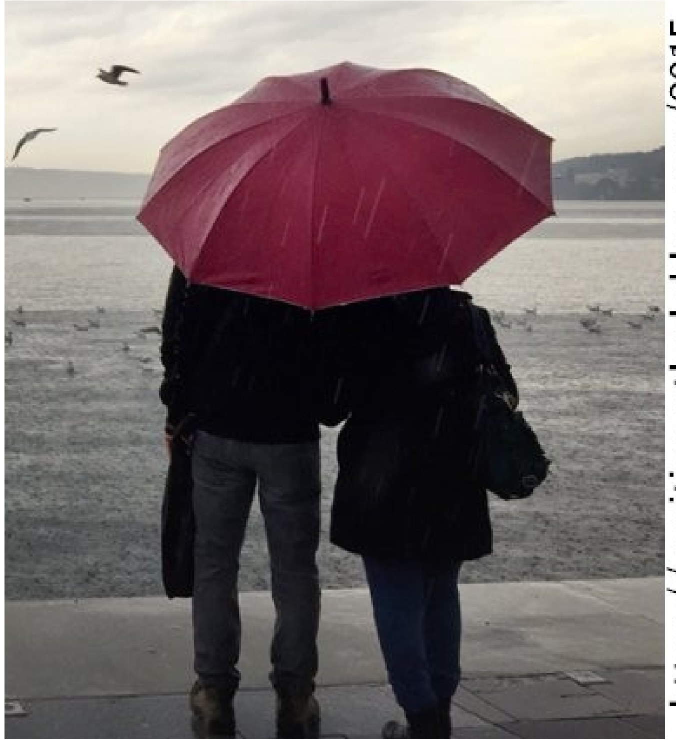
$$\langle X \rangle_{(\beta U)_1} = \frac{\int X \mathrm{e}^{-(\beta U)_1} \mathrm{d}\vec{r}^N}{\int \mathrm{e}^{-(\beta U)_1} \mathrm{d}\vec{r}^N} = \frac{\int X \mathrm{e}^{-(\beta U)_0}\, \mathrm{e}^{-\Delta(\beta U)} \mathrm{d}\vec{r}^N}{\int \mathrm{e}^{-(\beta U)_0}\, \mathrm{e}^{-\Delta(\beta U)} \mathrm{d}\vec{r}^N} = \frac{\langle X \mathrm{e}^{-\Delta(\beta U)} \rangle_0}{\langle \mathrm{e}^{-\Delta(\beta U)} \rangle_0}$$

Helmholtz energy:

$$\begin{aligned}
\Delta(\beta F_{\mathrm{res}}) &= \beta_1 F_{\mathrm{res}}((\beta U)_1) - \beta_0 F_{\mathrm{res}}((\beta U)_0) \\
&= -\ln\left(\frac{Q_1}{Q_0}\right) = -\ln \frac{\int \mathrm{e}^{-(\beta U)_1} \mathrm{d}\vec{r}^N}{\int \mathrm{e}^{-(\beta U)_0} \mathrm{d}\vec{r}^N} \\
&= -\ln \frac{\int \mathrm{e}^{-(\beta U)_0}\, \mathrm{e}^{-\Delta(\beta U)} \mathrm{d}\vec{r}^N}{\int \mathrm{e}^{-(\beta U)_0} \mathrm{d}\vec{r}^N} = -\ln \langle \mathrm{e}^{-\Delta(\beta U)} \rangle_0 \\
&= \ln \langle \mathrm{e}^{+\Delta(\beta U)} \rangle_1
\end{aligned}$$

where the last equation follows from $0 \longleftrightarrow 1$ interchange

Non-Boltzmann sampling contd.



https://positiveoutlooksblog.com/2015/01/30/surviving-the-storm-together

- $\Delta(\beta U)$ must not be too large
- the thermodynamic integration is recovered for infinitesimally small $\Delta(\beta U)$:

$$\Delta(\beta F_{\text{res}}) = -\ln\langle e^{-\Delta(\beta U)}\rangle_0 \approx -\ln\langle 1 - \Delta(\beta U)\rangle_0 \approx \langle\Delta(\beta U)\rangle$$

$$\Rightarrow \quad \partial(\beta F_{\text{res}})/\partial\lambda = \langle\partial\Delta(\beta U)/\partial\lambda\rangle_\lambda$$

Umbrella sampling

The system in the middle is sampled: $\text{mid} = (\beta U)_0 + \Delta(\beta U)/2 = (\beta_0 U_0 + \beta_1 U_1)/2$:

$$\Delta(\beta F_{\text{res}}) = \ln\langle e^{+\Delta(\beta U)/2}\rangle_{\text{mid}} - \ln\langle e^{-\Delta(\beta U)/2}\rangle_{\text{mid}}$$

Widom particle insertion method I

Open system

$$\mathrm{d}F = -S\mathrm{d}T - P\mathrm{d}V + \mu\mathrm{d}N$$

$$\beta\mu = \left(\frac{\partial(\beta F)}{\partial N}\right)_{V,T} = -\left(\frac{\partial \ln Z_N}{\partial N}\right)_{V,T}$$

$$\beta\mu_{\mathrm{res}} = \left(\frac{\partial(\beta F_{\mathrm{res}})}{\partial N}\right)_{V,T} = -\left(\frac{\partial \ln(Q_{\mathrm{N}}/V^N)}{\partial N}\right)_{V,T} \approx -\left(\ln\frac{Q_{N+1}}{V^{N+1}} - \ln\frac{Q_N}{V^N}\right)$$

$$\exp(-\beta\mu_{\mathrm{res}}) = \frac{1}{V}\frac{Q_{N+1}}{Q_N}$$

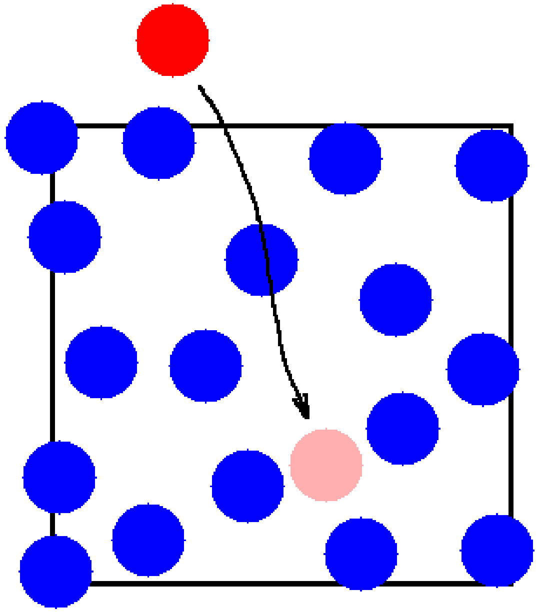
Or for the full chemical potential:

$$\mathrm{e}^{-\beta\mu} = \frac{Z_{N+1}}{Z_N} = \frac{1}{(N+1)\Lambda^3}\frac{Q_{N+1}}{Q_N} \approx \frac{1}{N\Lambda^3}\frac{Q_{N+1}}{Q_N}$$

then by subtracting $\mu^{\mathrm{id}} = k_{\mathrm{B}}T\ln\left(\frac{N\Lambda^3}{V}\right)$ we get the same $\mu_{\mathrm{res}} = \mu - \mu^{\mathrm{id}}$

Widom particle insertion method II

$$\exp(-\beta\mu_{\rm res}) = \frac{1}{V}\frac{Q_{N+1}}{Q_N}$$



$$N \to N+1 \qquad U_{N+1} = U_N + \Psi(N)$$

$$\frac{1}{V}\frac{Q_{N+1}}{Q_N} = \frac{1}{VQ_N}\int \exp(-\beta U_N - \beta\Psi)\mathrm{d}\vec{r}_1 \ldots \mathrm{d}\vec{r}_{N+1}$$

$$= \frac{1}{V}\int \langle \mathrm{e}^{-\beta\Psi}\rangle_N \mathrm{d}\vec{r}_{N+1}$$

$$\exp(-\beta\mu_{\rm res}) = \frac{1}{V}\int \langle \mathrm{e}^{-\beta\Psi}\rangle_N \mathrm{d}\vec{r}_{N+1} = \Big\langle \langle \mathrm{e}^{-\beta\Psi}\rangle_N \Big\rangle_{\text{random } \vec{r}_{N+1}}$$

$\frac{1}{V}\int X \mathrm{d}\vec{r}_{N+1} = \langle X\rangle_{\text{random } \vec{r}_{N+1}}$ = mean value of X over positions of the $(N+1)$-th particle in volume V, calculated by MC integration (random shooting)

$(N+1)$-th particle does not influence the system – it is virtual (fictitious, ghost)

Problem: dense systems, large solutes
Remedy: gradual insertion (thermodynamic integration or by finite steps)

Similar: solute insertion ⇒ solubility, Henry constant

Reversible work by integrating the mean force

From thermodynamics:

$$\Delta\mu_i = -\int_{\vec{r}_i(1)}^{\vec{r}_i(2)} \langle \vec{f}_i \rangle \cdot \mathrm{d}\vec{r}_i$$

where $\vec{f}_i$ is the force acting on particle i and $U_i(\vec{r}_i)$ is its potential

Molecules: the force applies to the center of mass or other reference point

Example: