

● Temperature (NVE MD):

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

$U = U(r^N)$ = potential
 $E = E(T, V)$ = internal energy

● Internal energy:

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

res = residual
see next slide

● Pressure

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

$$P = -\left(\frac{\partial F}{\partial V}\right)_T, \quad F = -k_{\text{B}}T \ln \frac{Q_{\text{NVT}}}{N! \Lambda^{3N}}, \quad Q_{\text{NVT}} = \int_{V^N} \exp(-\beta U) d\vec{r}^N$$

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

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

where the derivative $\partial U(V^{1/3} \vec{\xi}^N) / \partial V$ is calculated at constant $\vec{\xi}^N$, i.e., the whole configuration is uniformly shrank/swelled

= 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:

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

Notes:

de Broglie thermal wavelength:

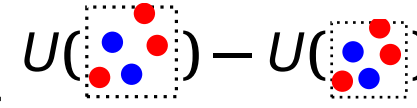
$$\Lambda = \frac{h}{\sqrt{2\pi m k_B T}}$$

chemical potential of ideal gas:

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

$$P = \frac{k_B T}{Q_{NVT}} \frac{\partial Q_{NVT}}{\partial V} = \frac{N}{V} k_B T - \left\langle \frac{\partial U(V^{1/3} \xi^N)}{\partial V} \right\rangle$$

Numerical derivative (for a selected series of configurations)

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


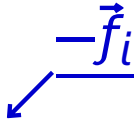
$$\frac{\partial U}{\partial V} = \frac{U(V + \Delta V) - U(V - \Delta V)}{2\Delta V} + \mathcal{O}(\Delta V^2)$$

Implementation: $U(V + \Delta V)$ means that the whole configuration (all distances) is swelled by the same ratio,

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

The scaled configuration is not included in the trajectory.

The derivative expanded:

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


The result is

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

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

In periodic boundary conditions

+

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

We need to know a partition function!

Formally (for the canonical partition function):

$$Q = \frac{\int e^{-\beta U} d\mathbf{r}^N}{1} = \frac{\int e^{-\beta U} d\mathbf{r}^N}{V^{-N} \int e^{-\beta U} e^{+\beta U} d\mathbf{r}^N} = \frac{V^N}{\langle e^{\beta U} \rangle}$$

... useless

- 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

Canonical ensemble – remember physical chemistry: ($E =$ internal energy)

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

- Numerically integrated – we must determine P , E in many points
- Start from a suitable known state (ideal gas, hard spheres, Lennard-Jones, Einstein crystal)

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 $\frac{\partial(\beta F)}{\partial \beta} = E$:

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

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

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

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

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

We want $\langle \beta U \rangle_1$, but we simulate $\langle \beta U \rangle_0$ (can change β/U /both)

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

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

Helmholtz energy:

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

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

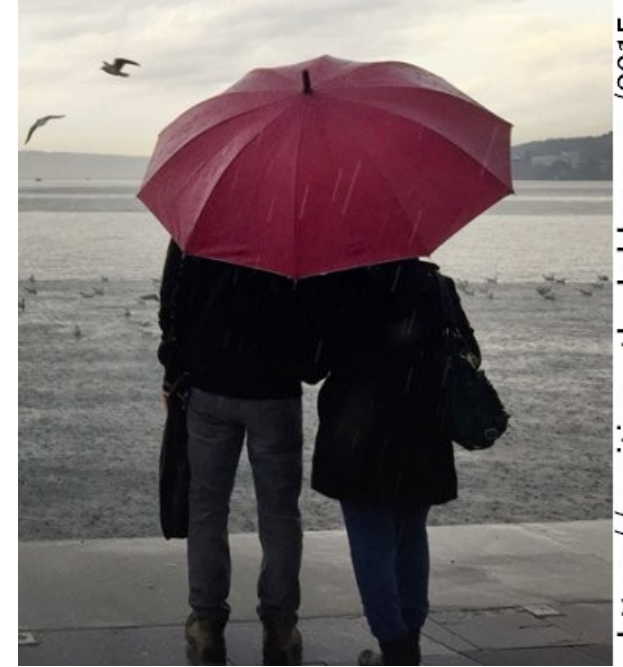
- $\Delta(\beta U)$ must not be too large
- the thermodynamic integration is recovered for infinitesimally small $\Delta(\beta U)$:

$$\Delta(\beta F_{\text{res}}) = -\ln \langle e^{-\Delta(\beta U)} \rangle_0 \approx \langle \Delta(\beta U) \rangle$$
$$\Rightarrow \partial(\beta F_{\text{res}}) / \partial \lambda = \langle \partial \Delta(\beta U) / \partial \lambda \rangle_\lambda$$

Umbrella sampling

The system in the middle is sampled:

$$\Delta(\beta F_{\text{res}}) = \ln \langle e^{+\beta \Delta U / 2} \rangle_{U_0 + \Delta U / 2} - \ln \langle e^{-\beta \Delta U / 2} \rangle_{U_0 + \Delta U / 2}$$



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

Open system

$$dF = -SdT - PdV + \mu dN$$

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

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

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

Or for the full chemical potential:

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

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

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

$$N \rightarrow N + 1 \quad U_{N+1} = U_N + \Psi(N)$$

$$\begin{aligned} \frac{1}{V} \frac{Q_{N+1}}{Q_N} &= \frac{1}{V Q_N} \int \exp(-\beta U_N - \beta \Psi) d\vec{r}_1 \dots d\vec{r}_{N+1} \\ &= \frac{1}{V} \int \langle e^{-\beta \Psi} \rangle_N d\vec{r}_{N+1} \end{aligned}$$

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

$\frac{1}{V} \int X d\vec{r}_{N+1} = \langle X \rangle_{\text{random } \vec{r}_{N+1}}$ = 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 \Rightarrow solubility, Henry constant

We have simulated $N = 500$ Ar atoms (Lennard-Jones: $\sigma = 3.405 \text{ \AA}$, $\epsilon/k_B = 119.8$ K) in a box of volume $V = 15.791 \text{ nm}^3$ at temperature $T = 150$ K. By the Widom method, we found that*

$$\exp(-\mu_{\text{res}}/k_B T) = 0.749(3)$$

Calculate μ° , the chemical potential of Ar with respect to the standard state of ideal gas at pressure $p^{\text{st}} = 1$ bar and temperature T .

Hints: $\mu_{\text{res}} = \mu - \mu(T, V)$ (N particles in volume V)

$\mu^\circ = \mu - \mu(T, V^\circ)$ ($V^\circ =$ volume of ideal gas of N particles at T, p^{st})

$$\begin{aligned} \mu_{\text{res}} &= 5.985 \times 10^{-22} \text{ J (per molecule)} \\ \sigma(\mu_{\text{res}}) &= k_B T \times (0.003/0.749) = 8.3 \times 10^{-24} \text{ J (std. error)} \\ V^\circ &= N k_B T / p^{\text{st}} = 10355 \text{ nm}^3 \\ \Delta\mu &\equiv \mu(15.791 \text{ nm}^3) - \mu(10355 \text{ nm}^3) = -T\Delta s \\ &= -k_B T \ln(15.791/10355) = 1.3432 \times 10^{-20} \text{ J} \\ \mu &= \mu_{\text{res}} + \Delta\mu = 1.4030(8) \times 10^{-20} \text{ J} \\ \mu &= 8.449(5) \text{ kJ mol}^{-1} \text{ (per mole)} \end{aligned}$$

*The value in parentheses is the estimated standard uncertainty in the units of the last significant digit.

Henry constant

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s07/2

Gas (2) dissolved in liquid (1), mole fraction in liquid $x_2 = N_2/(N_1 + N_2)$, $x_2 \ll 1$.
One form of the Henry law for partial pressure p_2 of (2) in equilibrium with solution:

$$p_2 = K_H x_2$$

By virtual insertion of one molecule ($N_2 = 1$) of (2) to pure liquid (1), we get the residual chemical potential of (2) at $x_2 = 1/(N_1 + 1) \approx 1/N_1$,

$$\mu_{\text{res},2} = \mu_2(x_2) - \mu_2^{\text{id}}(V)$$

$$\mu^{\text{id}}(V) = k_B T \ln \frac{N \Lambda^3}{V}$$

Because of equilibrium (don't forget that $N_2 = 1$),

$$\mu_2(x_2) = \mu^{\text{id}}(V_2) = k_B T \ln \frac{\Lambda_2^3}{V_2}$$

where V_2 is the volume corresponding to pressure p_2 ,

$$\mu^{\text{id}}(V_2) = \frac{1 k_B T}{p_2} = \frac{k_B T}{x_2 K_H} = \frac{k_B T N_1}{K_H}$$

Finally,

$$K_H = \rho_1 k_B T e^{\beta \mu_{\text{res},i}} = \frac{\rho_1 k_B T}{\langle \langle e^{-\beta \Psi} \rangle \rangle_{N_1} \text{random insertion of (2)}}$$

where $\rho_1 = N_1/V$ (number density of (1)).

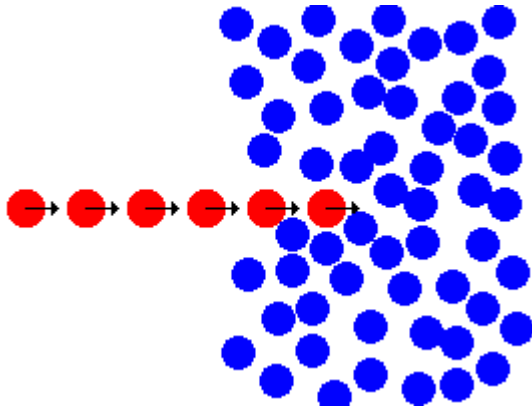
From thermodynamics:

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

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:



Let us define the **single-particle density** as

$$\rho_1(\vec{r}_1) = \frac{N}{Q_N} \int e^{-\beta U(\vec{r}_1, \dots, \vec{r}_N)} d\vec{r}_2 \dots d\vec{r}_N$$

- $\rho_1(\vec{r}_1)d\vec{r}_1$ is the probability of finding a particle (any one) in $d\vec{r}_1$
- extension to mixtures: $N/Q_N \rightarrow N_{\text{species}}/Q_N$

The **potential of mean force** is defined by

$$\bar{U}_1(\vec{r}_1) = -k_B T \ln[V\rho_1(\vec{r}_1)]$$

The corresponding force is

$$\bar{f}_i = - \left(\frac{\partial \bar{U}_1}{\partial \vec{r}_1} \right) = k_B T \frac{\partial \rho_1 / \partial \vec{r}_1}{\rho_1} = \left\langle - \left(\frac{\partial U}{\partial \vec{r}_1} \right) \right\rangle_{\vec{r}_2, \dots, \vec{r}_N} = \langle \vec{f}_1 \rangle_{\vec{r}_2, \dots, \vec{r}_N}$$

i.e., it is indeed the mean force on particle 1 held at fixed position \vec{r}_1 .

Note: Similarly, for a 2-particle distribution, which for a pair of particles in an isotropic fluid is $g(r)$, one defines the potential of mean force as:

$$\bar{U}_2(r) = -k_B T \ln[g(r)]$$