ΔU due to change of volume is demanding to calculate
trick for powerlaw potentials (such as LJ)

$$V_{LJ} = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

save seperately. V_{12}, V_6

$$r \to \left(\frac{V_{new}}{V_{old}}\right)^{1/3} r \quad , \text{ so}$$

$$V_{12} \to V_{12}\left(\frac{V_{new}}{V_{old}}\right)^{-4}$$

$$V_6 \to V_6\left(\frac{V_{new}}{V_{old}}\right)^{-2}$$

end ...

---

grand canonical μVT | i.e small system c bigger system

normal NVT or
- insert / remove particles

careful with normalisation again $\quad \propto \frac{V^N}{\Lambda^{3N} N!}\int dr_1 \ldots dr_N \exp[-\beta(U-\mu N)]$

Λ de Broglie wavelength

insert at random position / remove random particle } with equal prob. $\Rightarrow$ symmetry

$$P(N \to N+1) = \min\left(1, \frac{V}{\Lambda^3 (N+1)} \exp[-\beta(\mu - \Delta U)]\right)$$

$$P(N \to N-1) = \min\left(1, \frac{\Lambda^3 N}{V} \exp[-\beta(\mu + \Delta U)]\right)$$

one = 1 other not

check detailed balance

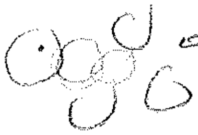
$$P(N \to N+1)\frac{V^N}{\Lambda^{3N} N!}\exp[-\beta(U_N - \mu N)]$$

$$= P(N+1 \to N)\frac{V^{N+1}}{\Lambda^{3(N+1)}(N+1)!}\exp[-\beta(U_{N+1} - \mu(N+1))]$$

$\Rightarrow$ everything matches nicely.

problem: at high density $\Rightarrow \Delta U$ very big $\Rightarrow$ low acceptance rate

solution: position dependent insertion rate (trick with symmetry)



$\leftarrow$ high prob of overlap.

can also use for multi component mixture $\mu_1 \mu_2$ (chemical reactions)
(take care to insert / remove species with same prob)
, select species first

---

combine for μPT

Averages continued:
Free energy calculations

FK 7.029

(37)

- cannot express directly as average.

Free energy differences

(Thermodynamic integration)

option ① $\left.\frac{\partial F}{\partial V}\right|_{N,T} = -p$ or $\frac{\partial F/T}{\partial 1/T} = E$ etc...

$$\Delta F = \int_{V_0}^{V_1} dV\,(-p)$$

option ② $F = -\frac{1}{\beta}\log Z$ (Overlapping distribution method)

$Z_1 = \dots \int \exp(-\beta U_1)$

$Z_0 = \dots \int \exp(-\beta U_0)$ ← reference system

$$\log\frac{Z_1}{Z_0} = -(\beta_1 F_1 - \beta_0 F_0) = \log\frac{\int \exp(-\beta(U_1-U_0)-\beta U_0)}{\int \exp(-\beta U_0)}$$

$$= \log\left\langle \exp[-\beta(U_1-U_0)]\right\rangle_{\text{system } 0}.$$

· only works if dists overlap sufficiently
otherwise: need a chain of differences

umbrella sampling

option ③ acceptance ratio

etc....

Transport coefficients: Green-Kubo (autocorrelation functions)

Chemical potential

particle insertion

$$Z = \underbrace{\frac{V^N}{\Lambda^{dN} N!}}_{Z_{ideal}} \int ds \exp(-\beta U)$$

reference to ideal gas

$F = -\frac{1}{\beta}\log Z = F_{ideal} + F_{excess}$.

$\mu = F(N+1) - F(N)$

$$\mu = -\frac{1}{\beta}\left(Z_{ideal}(N+1) - Z_{ideal}(N)\right) - \frac{1}{\beta}\frac{\int ds^{N+1}\exp(-\beta U)}{\int ds^N \exp(-\beta U)}$$

analytically known

$= \mu_{ideal} + \mu_{excess}$.

$\mu_{excess} = -\frac{1}{\beta}\log\int ds\,\langle\exp(-\beta\Delta U)\rangle$ (not) adding a particle at a random location