

# Free Energy

- Ch 7

- why are free energies important?
- when we are interested in the relative stability of several phases.
- The second law of thermodynamics: for a closed system with energy  $E$ , volume  $V$ , and number of particles  $N$ , (NVE) the entropy  $S$  is at a maximum when the system is in equilibrium.
- if  $NVT$  are fixed: Helmholtz free energy  $F \equiv E - TS$  is at a minimum in equilibrium.
- NPT: the Gibbs free energy  $G \equiv F + PV$  is at a minimum.

2 phases  $\alpha$  and  $\beta$  in equilibrium:

- at a given temperature and density, we should simply compare the Helmholtz free energies  $F_\alpha$  and  $F_\beta$  of these phases.

it is not possible to measure the free energy or entropy directly in a simulation!

Entropy, free energy, and related quantities are not simply averages of functions of the phase space coordinates of the system.

Rather they are directly related to the partition function

The partition function is NOT calculated in a simulation.

For instance, in classical statistical mechanics, the Helmholtz free energy

$$F = -kT \ln Q(N, V, T)$$

Same for  $G = U - TS + PV$

S, F, G can not be directly measured in an experiment!

Can be calculated from measured properties: P(V,T), E

$$\left. \frac{\partial F}{\partial V} \right|_{NT} = -P$$
$$\left. \frac{\partial F / T}{\partial 1 / T} \right|_{VN} = E$$

For example, to compute the F for a system at a given temperature and density, we should find a reversible path in the V-T plane that links the state under consideration to a state of **known** free energy. The change in F along that path can then simply be evaluated by thermodynamic integration.

There are only very few thermodynamic states for which the free energy of a substance is **known**, for example: the ideal gas

The free energy of a liquid can be integrated from the ideal gas if we measured  $P(V,T)$

### Artificial thermodynamic integration

In computer simulations we are not limited to using a physical thermodynamic integration path

For example, if we know the free energy of the Lennard-Jones fluid, we can determine the free energy of the Stockmayer fluid by turning on the dipolar interactions: the integration path goes from zero term to finite dipolar term.

$$\text{Stockmayer fluid : } U = U_{\text{LJ}} + U_{\text{dipolar}}$$

Let us consider an N-particle system with a potential energy function  $U$ .

$$U = U(\lambda) = U = (1 - \lambda) U_{LJ} + \lambda U_{\text{dipolar}}$$

$\lambda$  : parameter that turns on the dipolar interactions:

for  $\lambda = 0$ ,  $U = U_{LJ}$  (system I)

$\lambda = 1$ , Stockmayer (system II)

$$U(\lambda) = U = (1 - \lambda) U_I + \lambda U_{II}$$

We assume that we know  $U_I$  by analytical or numerical calculation

$$F_{\parallel} \quad F_{\perp}$$

$$F(\lambda = 1) - F(\lambda = 0) = \int_0^1 \frac{\partial F}{\partial \lambda} d\lambda$$

$$F(\lambda) = -kT \ln Q(\lambda)$$

$$Q = \int dr^{3N} \exp\{-\beta U(\lambda)\}$$

$$\frac{\partial F}{\partial \lambda} = -kT \frac{\partial \ln Q}{\partial \lambda} = -kT \int dr^{3N} (-\beta \partial U / \partial \lambda) \exp\{-\beta U(\lambda)\} / Q$$

$$= \left\langle \frac{\partial U}{\partial \lambda} \right\rangle$$

F can NOT be calculated as an ensemble average

$\Delta F$ : yes we can

# Chemical Potential

Particle insertion method

$$\mu = \left. \frac{\partial F}{\partial N} \right|_{VT}$$


$$F = -kT \ln Q$$

For large N:

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

$$= -kT \ln(Q_{N+1} / Q_N)$$




$$Q = \frac{V^N}{\lambda^{3N} N!} \int ds^{3N} \exp\{-kTU(s^{3N}, L)\}$$

$$= Q_{id} Q_{ex}$$

$$F = F_{id} + F_{ex}$$


$$\mu = \mu_{id} + \mu_{ex}$$



known

$$\mu_{ex} = -kT \ln(Q_{N+1} / Q_N)_{ex}$$

$$= -kT \ln \frac{\int ds^{3(N+1)} \exp(-\beta U(s^{3(N+1)}))}{\int ds^{3(N)} \exp(-\beta U(s^{3(N)}))}$$

$U_{N+1} = U_N + \Delta U$   interaction of (N+1)th particle with the other N

$$\mu_{ex} = -kT \ln \frac{\int ds^{3(N)} \exp(-\beta U(s^{3(N)})) \int ds_{N+1} \exp(-\beta \Delta U)}{\int ds^{3(N)} \exp(-\beta U(s^{3(N)}))}$$

$$= kT \ln \left\langle \int ds_{N+1} \exp(-\beta \Delta U) \right\rangle_N = kT \ln \int ds_{N+1} \langle \exp(-\beta \Delta U) \rangle_N$$

→ we can calculate  $\mu$  as an ensemble average

## Implementation Widom scheme:

- carry out a conventional constant-NVT Monte Carlo simulation on the system of  $N$  particles.
- At frequent intervals during this simulation, we randomly generate a coordinate  $S_{N+1}$ , uniformly over the unit cube.
- For  $(N+1)_{\text{th}}$  particle, compute  $\exp(-\beta \Delta U)$ .
- Average the  $\exp(-\beta \Delta U)$  over MC steps.
- The extra particle is NOT included in the system.

Algorithm:  
Subroutine WIDOM

```
xtest=box*ranf  
call ener(xtest,entest)  
wtest=wtest+exp(-beta*entest)  
return  
end
```

- This subroutine is usually called in sample.f
- Excess chemical potential:  $\beta \mu_{\text{ex}} = -\ln (w_{\text{test}} / M)$ , where M is the total number of test particle insertions.
- Subroutine ener calculates the energy of the test particle.
- The test particle insertion is virtual and is never accepted.

# Chemical potential in NPT

$$G_{NPT} = -kT \ln Z_{NPT}$$

$$Z_{NPT} = \int dV V^N \exp\{-\beta PV\} \int ds^{3N} \exp\{-\beta U(s^{3N}, V)\}$$

We must evaluate  $\mu = (\partial G / \partial N)_{PT}$ .

$$\mu = G(N+1, P, T) - G(N, P, T)$$

$$= \mu_{id}(P) + \mu_{ex}(P)$$

$$\text{with } \mu_{ex}(P) = -kT \ln \left\langle \frac{PV}{(N+1)kT} \int ds_{N+1} \exp\{-\beta \Delta U\} \right\rangle$$

- the ideal gas reference state at the same pressure, rather than at the same average density as the system under study.
- the fluctuating quantity that we are averaging is  $V \exp(-\beta \Delta U)$