Chapter 10

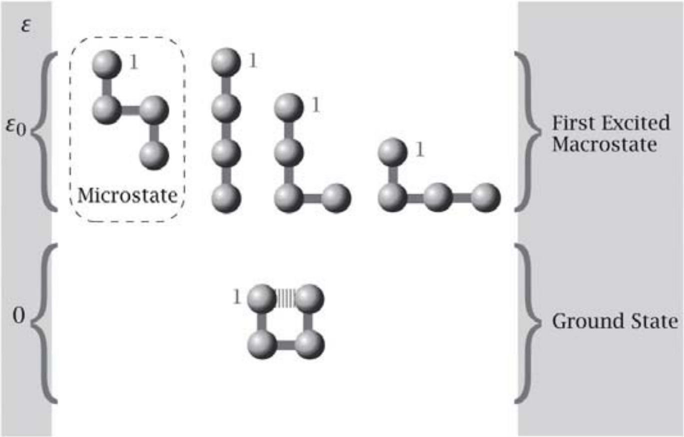


Figure 10.1 Molecular Driving Forces 2/e (© Garland Science 2011)

ε_j - independent particles

E_i - many-particle energy $\leftarrow$ if no interactions E_i is a sum of the occupied ε_j levels

---

what are probabilities p_j for E_j for fixed *N, V, T*

$dF = dU - TdS = 0$ at equilibrium

$$\frac{S}{k} = -\sum p_j \ell n p_j \qquad dS = -k\sum\left(1+\ell n p_j\right)dp_j$$

$$U = \left\langle E \right\rangle = \sum p_j E_j \qquad dU = \sum\left(E_j dp_j + p_j dE_j\right)$$

E_j does not depend on *T*

$\langle E \rangle$ does depend on *T*, due to the probabilities

$$dE_j = \left(\frac{\partial E_j}{\partial V}\right) dV + \left(\frac{\partial E_j}{\partial N}\right) dN = 0$$ since *N, V* held fixed

So $dU = \sum E_j dp_j$

$$d\langle E \rangle = dU = \delta q + \delta w = \delta q \,\Big|$$ fixed *V*

$$\Rightarrow \frac{\sum E_j dp_j}{heat}, \quad \frac{\sum p_j dE_j}{work}$$

$dF = d\langle E \rangle - TdS = 0$ subject to $\sum p_j = 1$

$$dF = \sum \left[E_j + kT\left(1 + \ell n p_j^*\right)\right] dp_j^* = 0$$

$$\ell n p_j^* = -\frac{E_j + \alpha}{kT} - 1$$

$$p_j^* = e^{-E_j/kT} e^{-(\alpha/kT+1)}$$

$$\sum p_j^* = 1$$

$$p_j^* = \frac{e^{-E_j/kT}}{\sum e^{-E_j/kT}} \qquad \frac{p_i^*}{p_j^*} = e^{-\left(E_i - E_j\right)/kT}$$

Q

Maxwell-Boltzmann Distribution

$$\varepsilon(U) = 1/2mv^2$$

$$p(v_x) = e^{-\varepsilon(v_x)/kT} \Big/ \int_0^\infty e^{-\varepsilon(v_x)/kT} = \frac{e^{-mv_x^2/2kT}}{\int_0^\infty e^{-mv_x^2/2kT}} dv_x$$

$$= \sqrt{\frac{m}{2\pi kT}} e^{-mv_x^2/2kT}$$

$$\left\langle v_x^2 \right\rangle = \sqrt{\frac{m}{2\pi kT}} \int_0^\infty v_x^2 e^{-mv_x^2/2kT} dv_x$$

$$\left\langle v_x^2 \right\rangle = \frac{kT}{m} \qquad \frac{1}{2} m \left\langle v_x^2 \right\rangle = \frac{1}{2} kT$$

$$\frac{1}{2} m \left\langle v^2 \right\rangle = \frac{3}{2} kT$$ ← The energy of an ideal gas

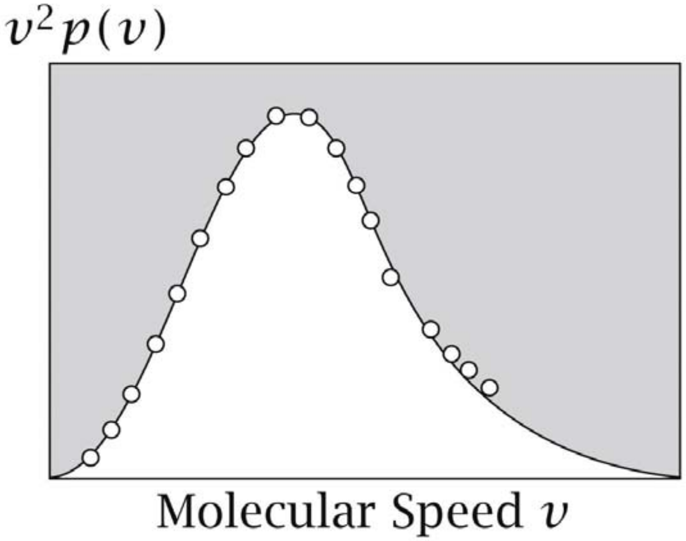


Figure 10.3 Molecular Driving Forces 2/e (© Garland Science 2011)

What information is in the partition function?

Q = # of states that are effectively accessible

E_j/kT is the “tuning parameter”

high *T* $p_j^* = 1/t$ $Q \to t$ # states

low *T* $p_1^* \to 1,$ $p_{i\neq 1}^* \to 0$ $Q \to 1$ only one level populated

---

Density of states

$W(E) =$ # of ways system can have energy *E*

$W(E) > 1 \Rightarrow$ degenerate level

4 bead chain

$$W(0) = 1 \quad \mathrm{W}(1) = 4 \quad Q = 1e^{-0/kT} + 4e^{-1/\mathrm{kT}}$$

$$Q = \sum_{\ell=1}^{\ell_{\max}} W(E_\ell) e^{-E_\ell(kT)}$$

$$p_\ell = \frac{1}{Q} W(E_\ell) e^{-E_\ell(kT)}$$

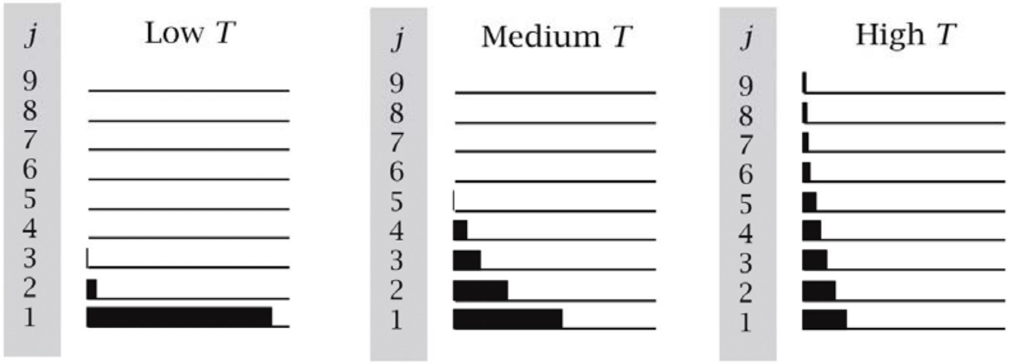


Figure 10.5 Molecular Driving Forces 2/e (© Garland Science 2011)

4 bead polymer problem

$$Q = 1 + 4e^{-E_\ell/kT}$$

$$p_c = \frac{1}{Q} \qquad p_0 = \frac{4e^{-E_0/kT}}{Q}$$

$$\Delta F = F_c - F_0 = 0 \ \text{ when } \ p_c = p_0$$

6 bead polymer chain with energies $0, \varepsilon_0, 2\varepsilon_0$

$$p(0) = 4/Q$$

$$p(1) = \frac{11e^{-2\varepsilon_0/kT}}{Q}$$

$$p(2) = \frac{21e^{-2\varepsilon_0/kT}}{Q}$$

Note that intermediate state becomes populated at intermediate *T*

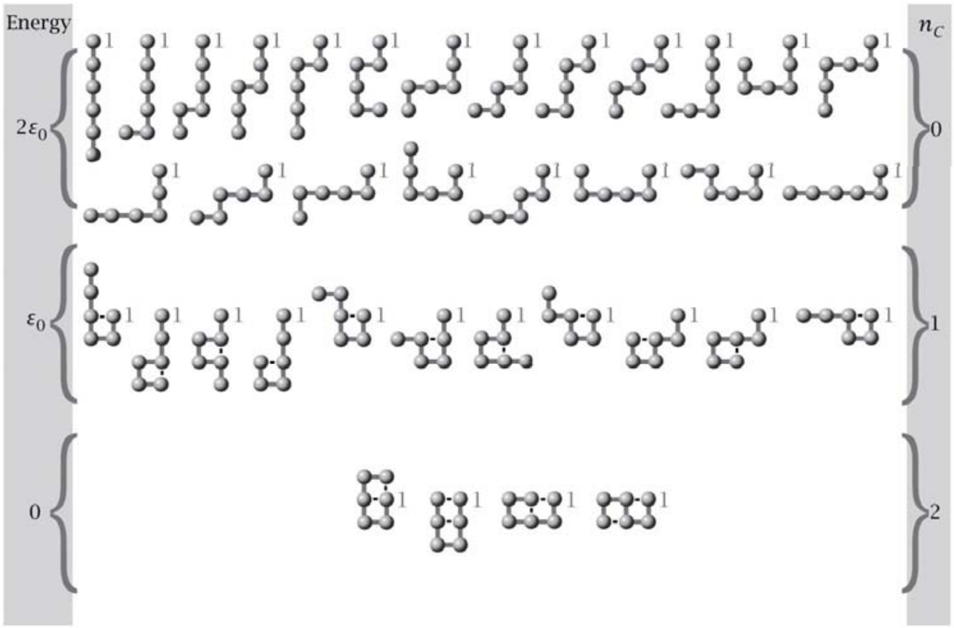


Figure 10.7 Molecular Drivin

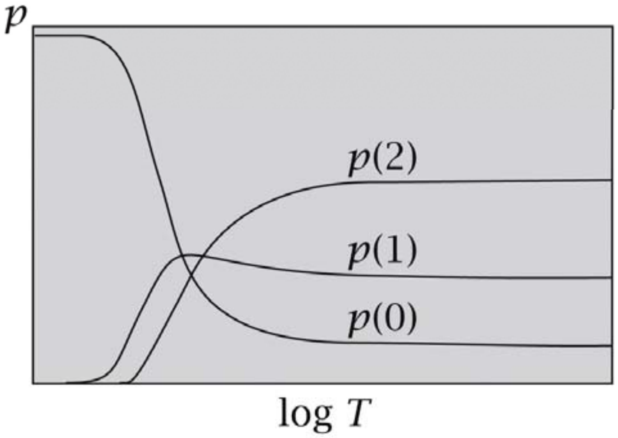


Figure 10.8 Molecular Driving Forces 2/e (© Garland Science 2011)

Again, assume particles do not interact

makes a difference if particles distinguishable or indistinguishable.

Two distinguishable particles

$E = \varepsilon_i^A + \varepsilon_j^B$ | two particles *A, B*

$$q_A = \sum e^{-\varepsilon_i^A/kT} \qquad q_B = \sum e^{-\varepsilon_m^B/kT}$$

$$Q = \sum e^{-E_j/kT} = \sum e^{-\left(\varepsilon_i^A + \varepsilon_m^B\right)/kT} = \sum_i e^{-\varepsilon_i^A/kT} \sum_j e^{-\varepsilon_m^B/kT}$$

$Q = q_A q_B$

In general, $Q = q^N$ | independent, distinguishable particles

Now consider independent indistinguishable particles

again, two particles

$$E_j = \varepsilon_i + \varepsilon_m$$

$$Q = \sum e^{-E_j/kT} = \sum_{i=1}^{t_1} \sum_{m=1}^{t_2} e^{-(\varepsilon_i + \varepsilon_m)/kT} \longleftarrow$$

can't factor as you don't know which particle is which

$$Q \approx q^2 / 2!$$

$$\mathrm{Q} \approx \mathrm{q}^N / N!$$ for *N* indistinguishable particles

---

Thermodynamics in terms of partition functions

$$U = \sum p_j^* E_j = \frac{1}{Q} \sum E_j e^{-\beta E_j} = \frac{-1}{Q} \frac{dQ}{d\beta} = -\frac{d\ell nQ}{d\beta}$$

$$\frac{U}{kT^2} = \frac{d\ell nQ}{dT}$$

$$\frac{d\beta}{dT} = \frac{-1}{kT^2}$$

If independent and distinguishable particles

$$\langle \varepsilon \rangle = \frac{U}{N} = \frac{kT^2}{N}\frac{d\ell nQ}{dT} = \frac{kT^2}{N}\frac{d\ell n(q^N)}{dT} = kT^2\frac{d\ell n(q)}{dT} = -\frac{d\ell n(q)}{d\beta}$$

$$\frac{S}{k} = -\sum p_j \ell n(p_j) = -\sum\left(\frac{1}{Q}e^{-E_j/kT}\right)\left[\ell n\left(\frac{1}{Q}\right)-\frac{E_j}{kT}\right]$$

$$S = k\ell nQ + \frac{U}{T} \qquad\qquad S = kN\ell n(q) + \frac{U}{T}$$

$$U = kT^2\left(\frac{\partial \ell nQ}{\partial T}\right)_{V,N}$$

$$S = k\ell nQ + \frac{U}{T} = k\ell nQ + kT\left(\frac{\partial \ell nQ}{\partial T}\right)_{V,N}$$

$$\boxed{F = U - TS = -kT\,\ell nQ}$$

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = -kT\left(\frac{\partial \ell nQ}{\partial N}\right)_{T,V}$$

$$p = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = kT\left(\frac{\partial \ell nQ}{\partial V}\right)_{T,N}$$

Schottky two-state model

$$q = 1 + e^{-\beta\varepsilon_0}$$

$$p_1^* = \frac{1}{q} \qquad p_2^* = \frac{e^{-\beta\varepsilon_0}}{q}$$

$$\langle\varepsilon\rangle = \frac{\varepsilon_0 e^{-\beta\varepsilon_0}}{1+e^{-\beta\varepsilon_0}}$$

$$C_V = N\frac{\partial\langle\varepsilon\rangle}{\partial T} = N\frac{\partial\langle\varepsilon\rangle}{\partial\langle\beta\rangle}\frac{d\beta}{dT} = \frac{-N}{kT^2}\left[\frac{-\varepsilon_0^2 e^{-\beta\varepsilon_0}}{\left(1+e^{-\beta\varepsilon_0}\right)^2}\right] = \frac{N\varepsilon_0^2}{kT^2}\frac{e^{-\beta\varepsilon_0}}{q^2}$$

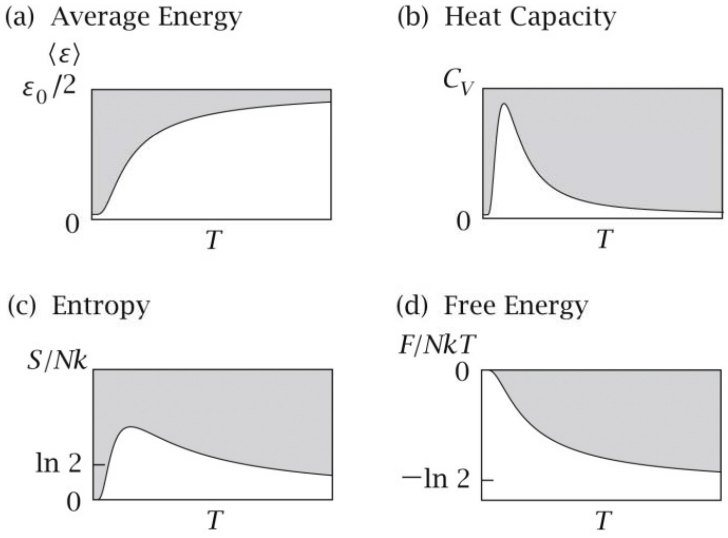
$$\langle\varepsilon^2\rangle = 0p_0 + \varepsilon_0^2 p_1 = \frac{\varepsilon_0^2 e^{-\beta\varepsilon_0}}{1+e^{-\beta\varepsilon_0}}$$

$$\langle\varepsilon\rangle^2 = \left(\frac{\varepsilon_0 e^{-\beta\varepsilon_0}}{1+e^{-\beta\varepsilon_0}}\right)^2$$

$$\langle\varepsilon^2\rangle - \langle\varepsilon\rangle^2 = \frac{\varepsilon_0^2 e^{-\beta\varepsilon_0}}{1+e^{-\beta\varepsilon_0}} - \frac{\varepsilon_0^2 e^{-2\beta\varepsilon_0}}{\left(1+e^{-\beta\varepsilon_0}\right)^2}$$

$$= \frac{\left(1+e^{-\beta\varepsilon_0}\right)\varepsilon_0^2 e^{-\beta\varepsilon_0} - \varepsilon_0^2 e^{-2\beta\varepsilon_0}}{\left(1+e^{-\beta\varepsilon_0}\right)^2}$$

$$= \frac{\varepsilon_0^2 e^{-\beta\varepsilon_0}}{\left(1+e^{-\beta\varepsilon_0}\right)^2} \longrightarrow C_V = \frac{N}{kT^2}\left(\langle\varepsilon^2\rangle - \langle\varepsilon\rangle^2\right)$$


(a) Average Energy

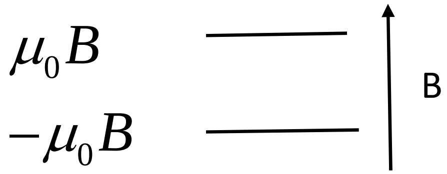
(b) Heat Capacity

(c) Entropy

(d) Free Energy

Figure 10.9 Molecular Driving Forces 2/e (© Garland Science 2011)

Paramagnetism – spins are aligned only when there is an applied magnetic field



$\mu_0 =$ magnetic dipole of atom

$$q = 1 + e^{-2\mu_0 B/kT}$$

defining the ground state as the zero of energy

parallel $p_1^* = \frac{1}{q}$ antiparallel $p_2^* = \frac{e^{-2\mu_0 B/kT}}{q}$

Average spin

$$\langle\mu\rangle = \sum \mu_j p_j^* = \mu_0 p_1^* - \mu_0 p_2^* = \mu_0 \frac{1-e^{-2\mu_0 B/kT}}{1+e^{-2\mu_0 B/kT}}$$

$$\frac{\mu_0 B}{kT} \to 0, \langle\mu\rangle \to \frac{\mu_0^2}{kT} B$$

$$\frac{\mu_0 B}{kT} \to \infty, \langle\mu\rangle \to \mu_0$$

$$\frac{\mu_0\left[1-\left(1-\frac{2\mu_0 B}{kT}\right)\right]}{1+1} = \frac{\mu_0^2 B}{kT}$$

Ensemble – two different contexts

1. What variables are held fixed?

   (U, V, N) microcanonical ensemble
   (T, V, N) canonical ensemble
   (T, p, N) isobaric-isothermal ensemble
   (T, V, μ) grand canonical ensemble

2. Ensemble: collection of all possible microstates

canonical: *T* fixed $\Rightarrow$ fix <*E*>
So *E* can fluctuate

microcanonical *E* is fixed – no fluctuations

In this case, we write *w(E, V, N)*
each microstate is equivalent $p_i^* = \frac{1}{W}$

$$\frac{S}{k} = -\sum_{i=1}^{W} p_i \ell n p_i = -\sum \frac{1}{W} \ell n \left(\frac{1}{W} \right) = \ell n W \left(E, \mathrm{V}, N \right)$$

$$-\frac{1}{W} \left[\ell n(1) - \ell n(W) \right] W = \ell n W$$