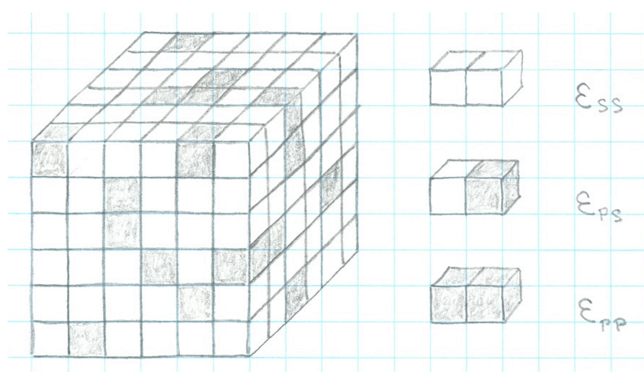
Model Free-Energy Density [pln32]

Lattice-gas model of two-component incompressible fluid with *internal energy* determined in mean-field approximation and *entropy* by maximum randomness in configuration space. The calculation of both ingredients ignores spatial correlations between solute particles (p) and solvent particles (s).

- Number of cells: $N = N_\mathrm{p} + N_\mathrm{s} = \phi N + (1-\phi)N$.
- Cell volume: $v_\mathrm{p} = v_\mathrm{s} \doteq v_\mathrm{c}$.
- Total volume: $V = N v_\mathrm{c}$.
- Volume fraction of solute: $\phi = N_\mathrm{p}/N$.
- Hardcore repulsion implied by single occupancy of all cells.
- VDW attraction via nearest-neighbor cell coupling: $\epsilon_{pp}, \epsilon_{ss}, \epsilon_{ps}$.
- Coordination number: z ($z = 6$ in cubic lattice shown).



Statistical mechanical task:

- Energy of microstate: $E_i = N_i^{(\mathrm{pp})}\epsilon_\mathrm{pp} + N_i^{(\mathrm{ss})}\epsilon_\mathrm{ss} + N_i^{(\mathrm{ps})}\epsilon_\mathrm{ps}$.
- Canonical partition function: $Z_N = \sum_i e^{-E_i/k_\mathrm{B}T}$.
- Helmholtz free energy: $F = -k_\mathrm{B}T \ln Z_N = U - TS$.
- Task here carried out by approximating U and S.

Average numbers of nearest-neighbor pairs (ignoring correlations):

- $\bar{N}_\mathrm{pp} = \frac{1}{2}N_\mathrm{p} z\phi = \frac{1}{2}Nz\phi^2$,
- $\bar{N}_\mathrm{ss} = \frac{1}{2}N_\mathrm{s} z(1-\phi) = \frac{1}{2}Nz(1-\phi)^2$,
- $\bar{N}_\mathrm{ps} = N_\mathrm{p} z(1-\phi) = Nz\phi(1-\phi)$.

Internal energy (relative to unmixed state):

$$
\begin{aligned}
U &= \frac{1}{2} z N \Big\{ \big[\epsilon_{\rm pp}\phi^2 + \epsilon_{\rm ss}(1-\phi)^2 + 2\epsilon_{\rm ps}\phi(1-\phi)\big] - \big[\epsilon_{\rm pp}\phi + \epsilon_{\rm ss}(1-\phi)\big] \Big\} \\
&= -\frac{1}{2} z N \big[\underbrace{\epsilon_{\rm pp} + \epsilon_{\rm ss} - 2\epsilon_{\rm ps}}_{\Delta\epsilon} \big] \phi(1-\phi).
\end{aligned}
$$

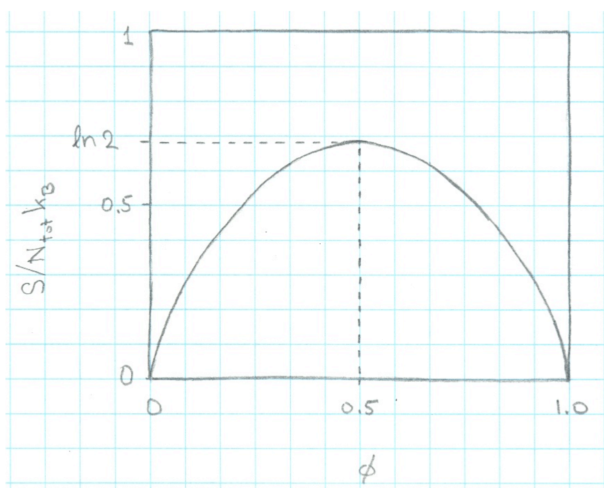
Energetically, $\Delta\epsilon > 0$ favors mixing and $\Delta\epsilon < 0$ favors unmixing.

Multiplicity of microstates: $W = \begin{pmatrix} N \\ N_{\rm p} \end{pmatrix} = \dfrac{N!}{N_{\rm p}!(N-N_{\rm p})!}$.

Entropy of mixing (ignoring correlations): $S = k_{\rm B} \ln W$.

Use Stirling approx., $\ln N! \simeq N \ln N - N$, and volume fraction, $\phi = N_{\rm p}/N$.

$$
\begin{aligned}
S &= N k_{\rm B} \big[\ln N - 1 - \phi \ln N_{\rm p} + \phi - (1-\phi)\ln(N - N_{\rm p}) + 1 - \phi \big] \\
&= N k_{\rm B} \big[-\phi \ln \phi - (1-\phi)\ln(1-\phi) \big].
\end{aligned}
$$



Helmholtz free-energy density, $f(T,\phi) \doteq [U - TS]/V$:

$$
f(T,\phi) = \frac{k_{\rm B}T}{v_{\rm c}} \big[\phi \ln \phi + (1-\phi)\ln(1-\phi) + \chi\phi(1-\phi) \big], \quad \chi \doteq -\frac{z}{2k_{\rm B}T}\Delta\epsilon.
$$

Typically, $\chi > 0$ is realized. Overall then (energetically and entropically), low χ (high T) favors mixing and high χ (low T) favors unmixing.

[extracted from Doi 2013]