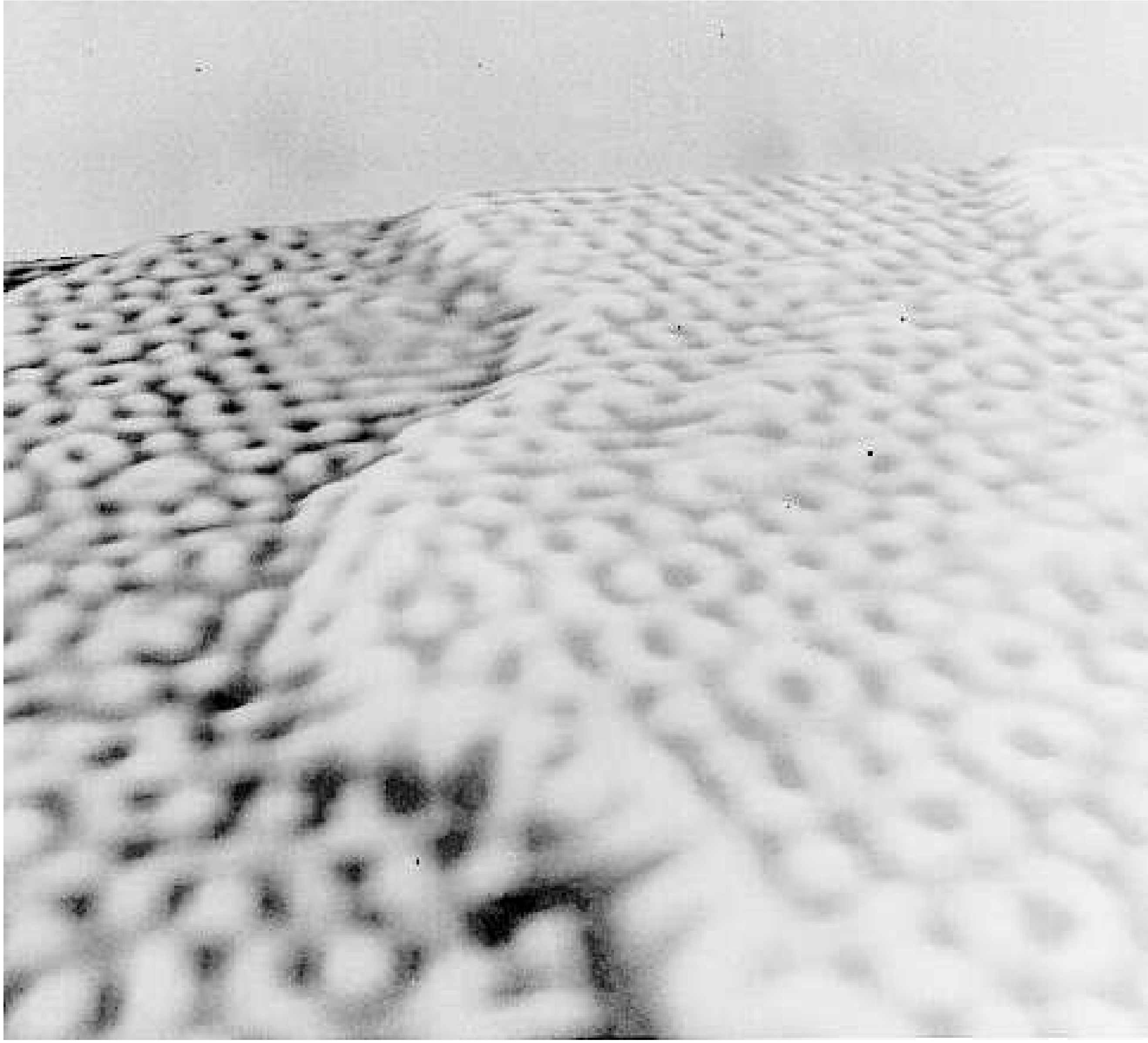
Complex Structures



Entropy always favors mixing things together:

$$\binom{N}{M} = \frac{N!}{M!(N-M)!} \approx \frac{N^M}{M!}, \tag{L1}$$

$$c = M/N, \tag{L2}$$

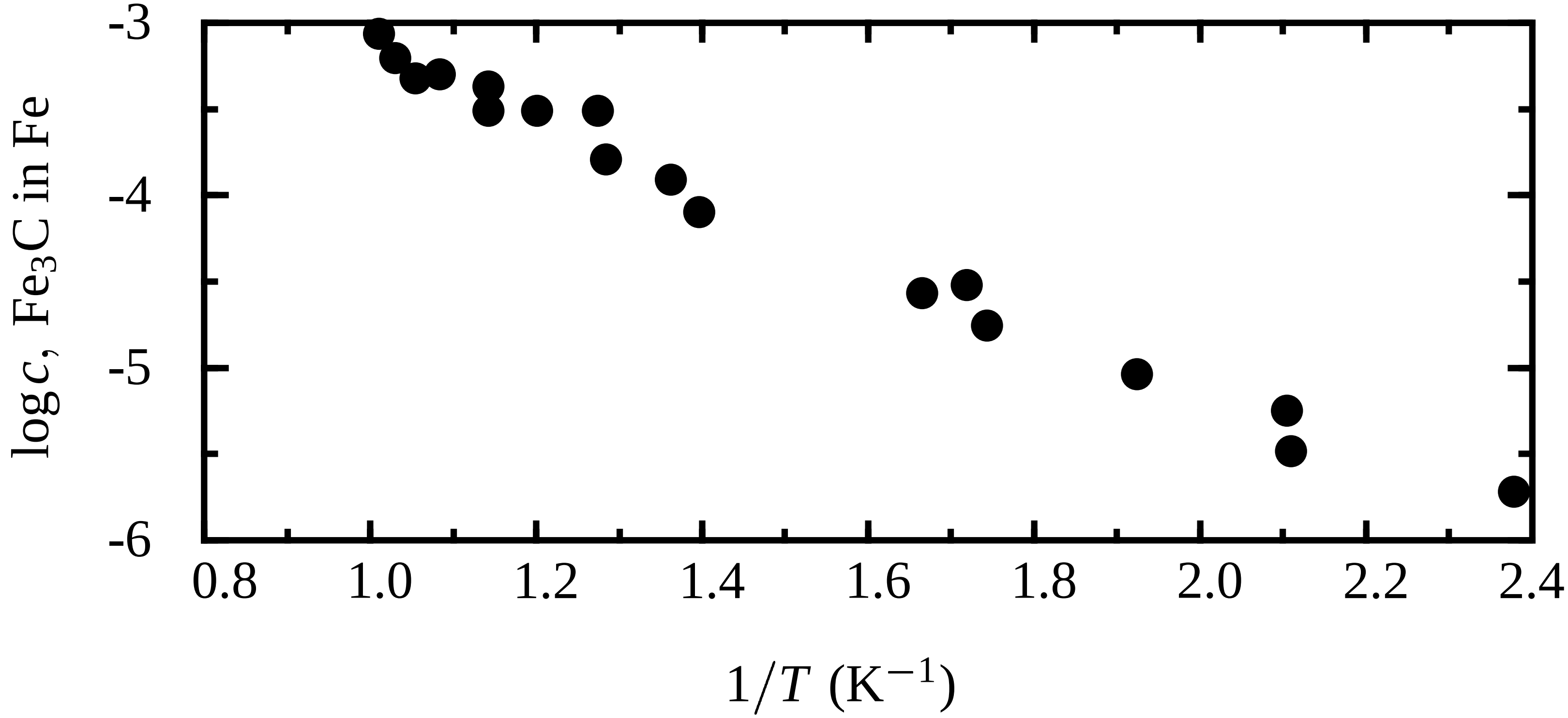
is

$$k_B \ln(N^M/M!) \approx -k_B N(c \ln c - c). \tag{L3}$$

$$\mathcal{F} = \mathcal{E} - TS = N[c\epsilon + k_B T c \ln c - k_B T c], \tag{L4}$$

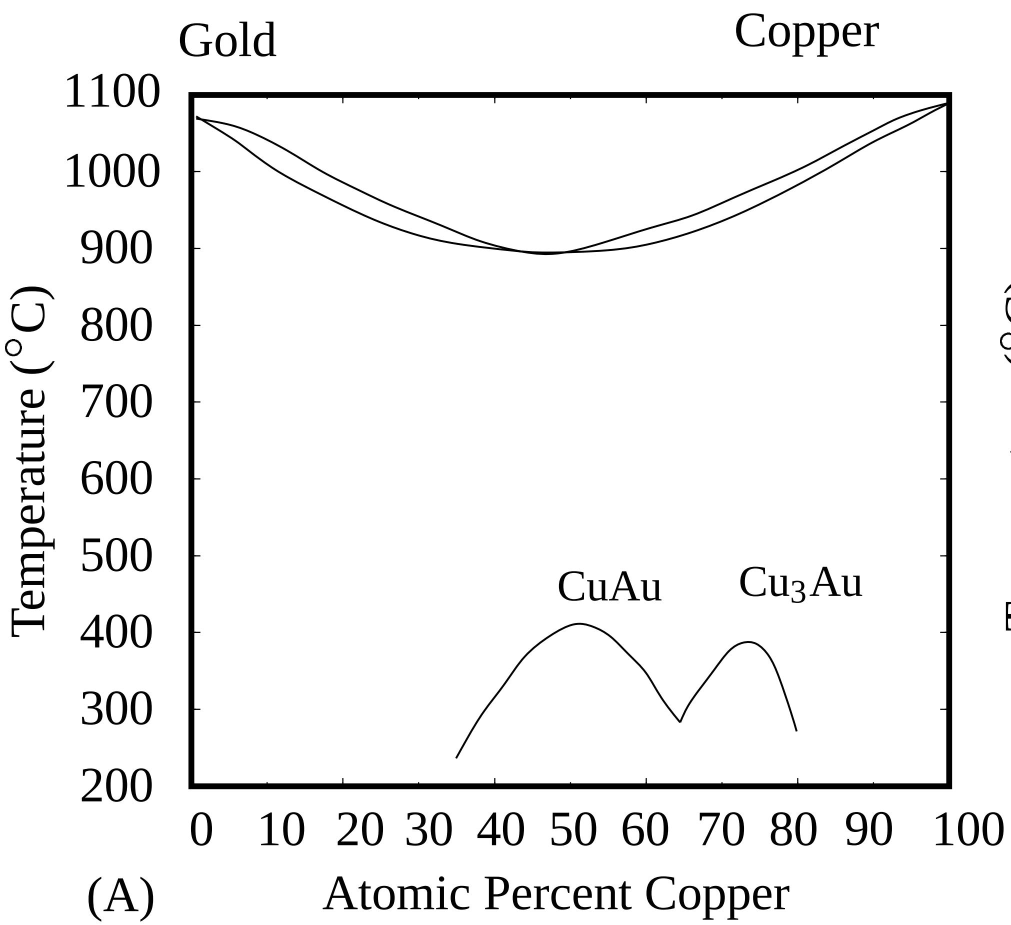
$$c \sim e^{-\epsilon/k_B T}. \tag{L5}$$

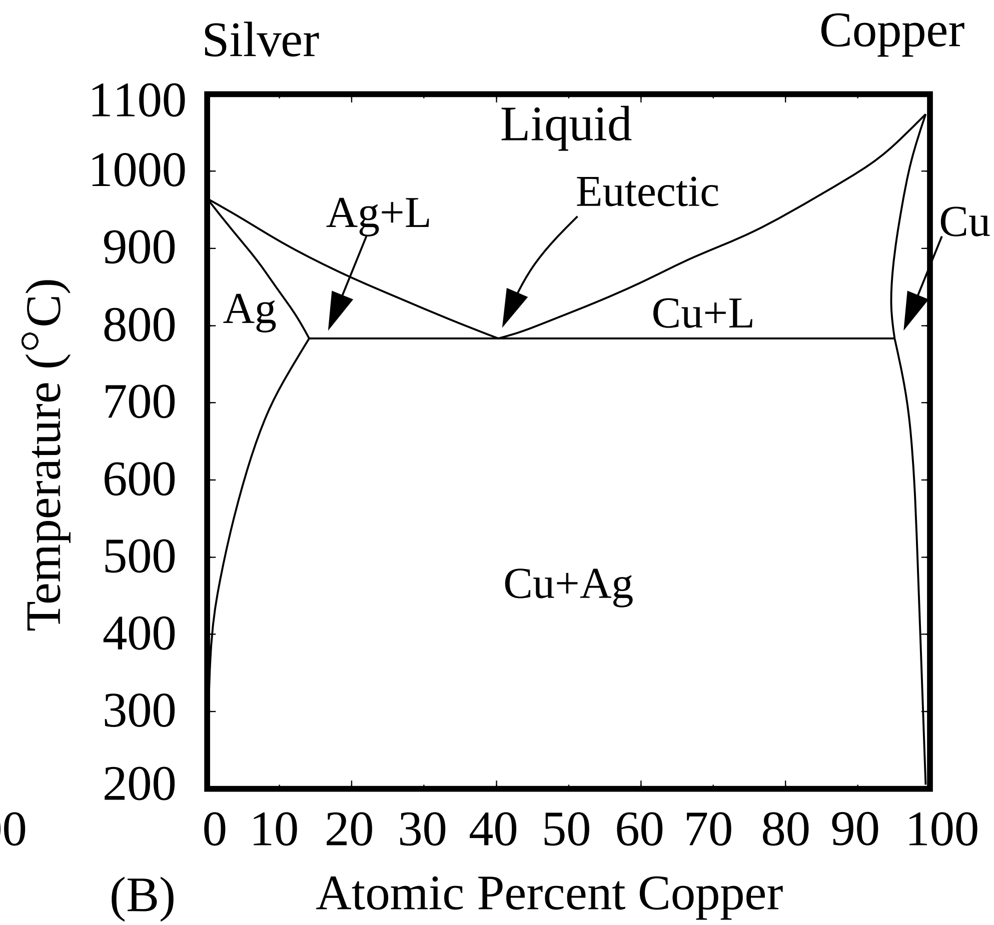
Alloys



Flynn (1972)

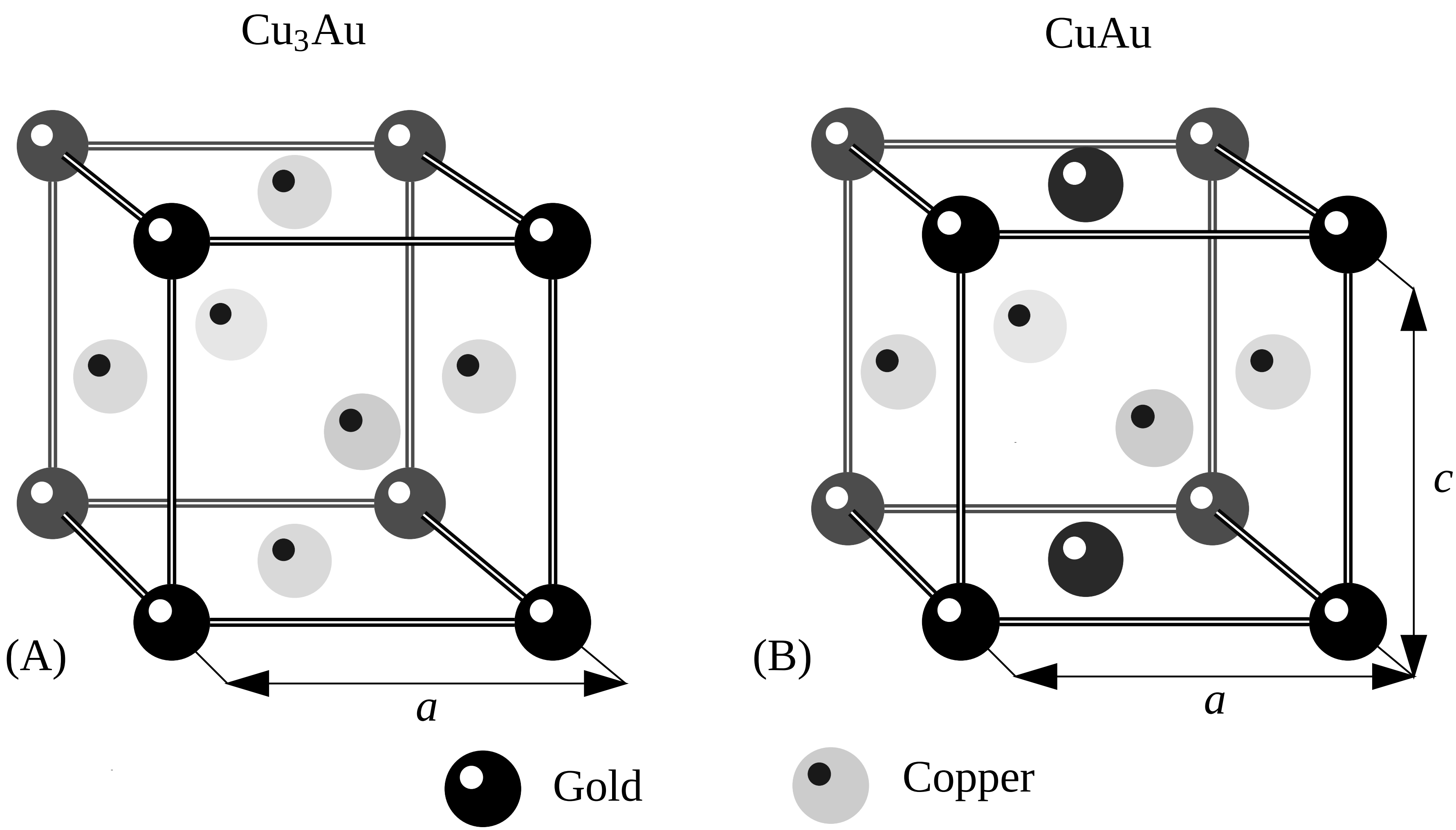
Alloys





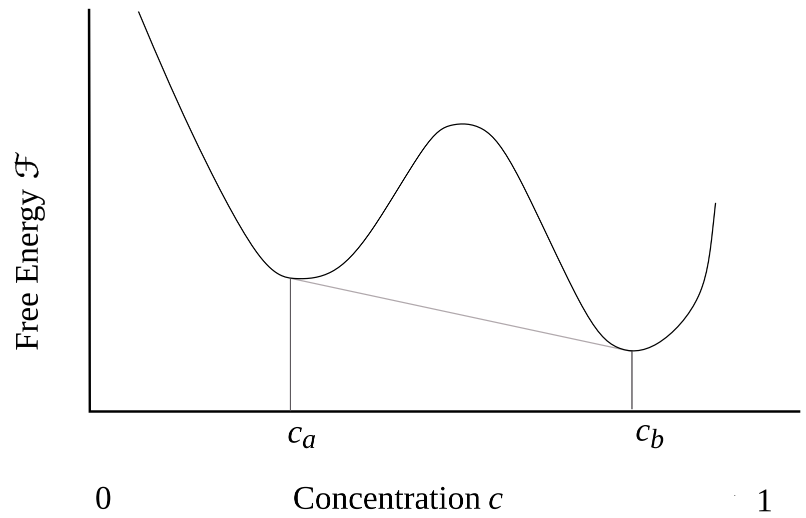
Hansen (1958)

Superlattices



(A) A 3:1 mixture of copper and gold (B) Equal mixtures. Lattice constant *c* is 7% smaller than *a*.

Phase Separation

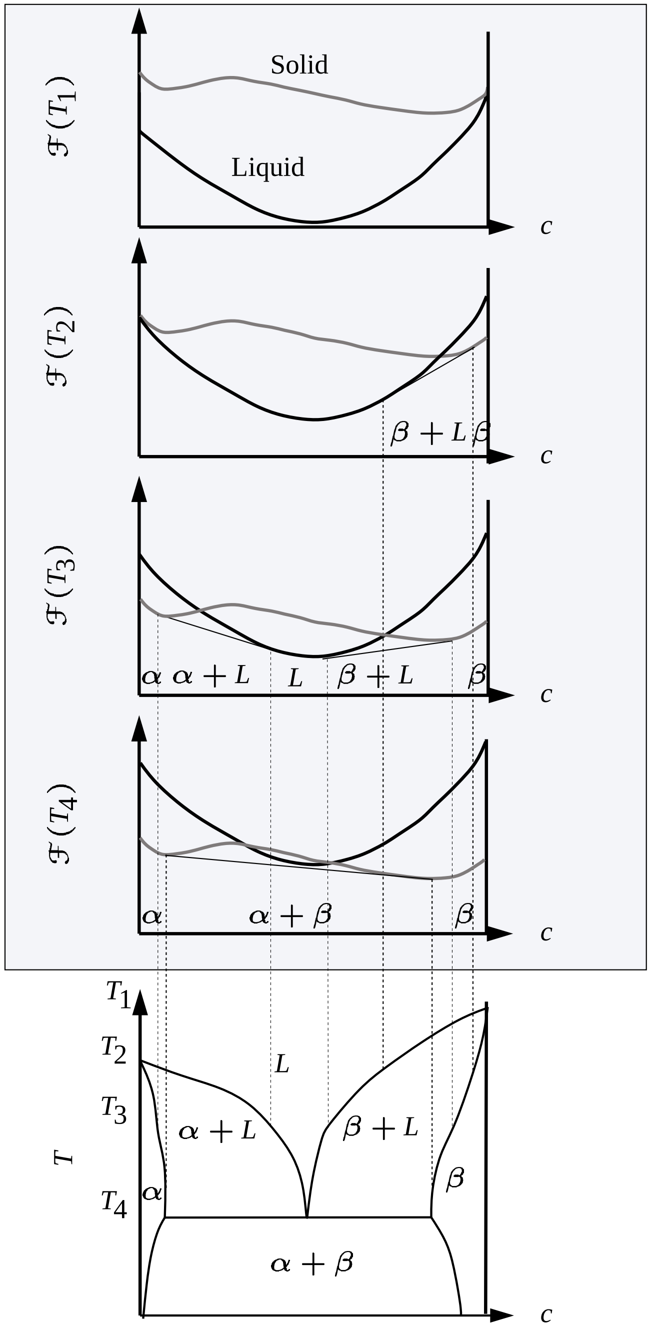


$$\mathcal{F}_{\rm ps} = f\mathcal{F}(c_a) + (1 - f)\mathcal{F}(c_b), \tag{L6}$$

(L7)

$$\Rightarrow \mathcal{F}_{\rm ps} = \frac{c - c_b}{c_a - c_b}\mathcal{F}(c_a) + \frac{c_a - c}{c_a - c_b}\mathcal{F}(c_b). \tag{L8}$$

Phase Separation



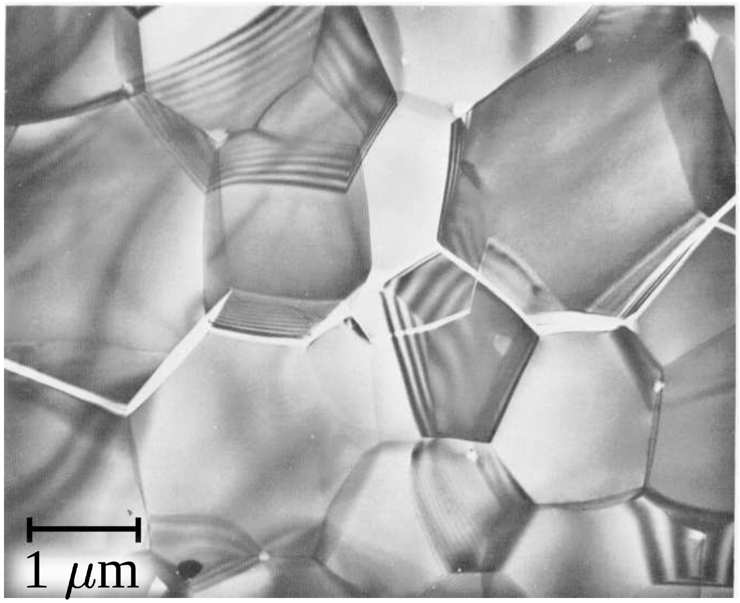
At sufficiently high temperatures, the liquid phase is of lower free energy at all concentrations c than the solid.

At this temperature, the liquid L is lower in energy to the left, but coexists with solid of type β towards the right, and β is stable for sufficiently high concentrations.

Now solid of type α is stable for low values of c, β is stable for high values, liquid is stable for a small range in the middle, and there are two coexistence regions.

Only solid phases are stable. These can be pure α, pure β, or mixtures $\alpha + \beta$ of the two.

Grains



Due to B. Hockey, attributed to E. Fuller, and published by R. Thomson (1986)

$$\vec{j} = -\mathcal{D}\vec{\nabla}c. \tag{L9}$$

$$\frac{\partial c}{\partial t} = \mathcal{D}\nabla^2 c \tag{L10}$$

$$\vec{F}_l = -\frac{\partial \mathcal{E}}{\partial \vec{R}_l}, \tag{L11}$$

$$m_l \frac{d^2 \vec{R}_l}{dt^2} = \vec{F}_l. \tag{L12}$$

$$\vec{R}_l^{n+1} = 2\vec{R}_l^n - \vec{R}_l^{n-1} + \frac{\vec{F}_l^n}{m_l} dt^2 \tag{L13}$$

with

$$\vec{F}_l^n = \vec{F}_l(\vec{R}_1^n \vec{R}_2^n \ldots \vec{R}_N^n) \tag{L14}$$

Order parameters

$$n_2(\vec{r}_1,\vec{r}_2;t) = \left\langle \sum_{l\neq l'} \delta(\vec{r}_1 - \vec{R}_l(0))\delta(\vec{r}_2 - \vec{R}_{l'}(t)) \right\rangle . \tag{L15}$$

$$S(\vec{q}) \equiv \frac{I}{NI_{\text{atom}}} \tag{L16}$$

$$= 1 + \frac{1}{N}\int d\vec{r}_1\, d\vec{r}_2\, n_2(\vec{r}_1,\vec{r}_2;0)e^{i\vec{q}\cdot(\vec{r}_1-\vec{r}_2)} \tag{L19}$$

where

$$n_2(\vec{q}) = \frac{1}{\mathcal{V}}\int d\vec{r}d\vec{r}'\, n_2(\vec{r}+\vec{r}',\vec{r};0)e^{i\vec{q}\cdot\vec{r}'} . \tag{L20}$$

Long- and Short-Range Order

Long–range order in crystals...

$$\mathcal{O}_{\vec{K}} = \frac{\mathcal{V}}{N^2} n_2(\vec{K}). \tag{L21}$$

Short–range order in liquids...

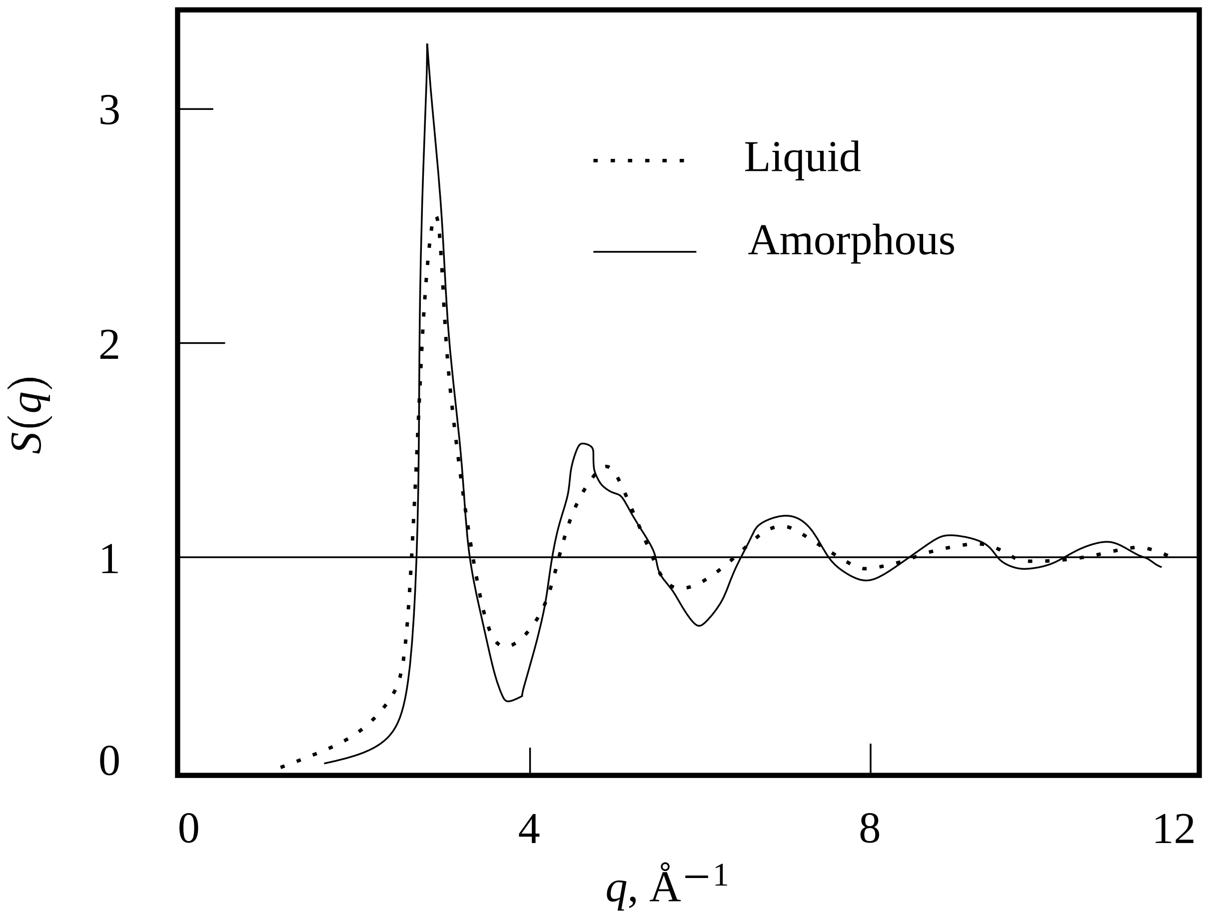
$$g(r) \equiv \frac{n_2(r)}{n^2}. \tag{L22}$$

$$S(\vec{q}) = 1 + n \int d\vec{r}\, g(r) e^{i\vec{q}\cdot\vec{r}} \tag{L23}$$

$$= 1 + n \int d\vec{r}\, (g(r) - 1) e^{i\vec{q}\cdot\vec{r}} + n \int d\vec{r}\, e^{i\vec{q}\cdot\vec{r}} \tag{L24}$$

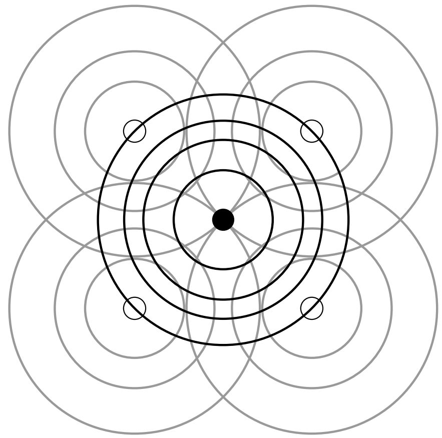
$$\approx 1 + n \int d\vec{r}\, e^{i\vec{q}\cdot\vec{r}} (g(r) - 1). \tag{L25}$$

Long- and Short-Range Order



$$z = n \int_0^{\text{first peak}} dr\, 4\pi r^2 g(r), \qquad \text{(L26)}$$

Extended X-Ray Absorption Fine Structure (EXAFS)



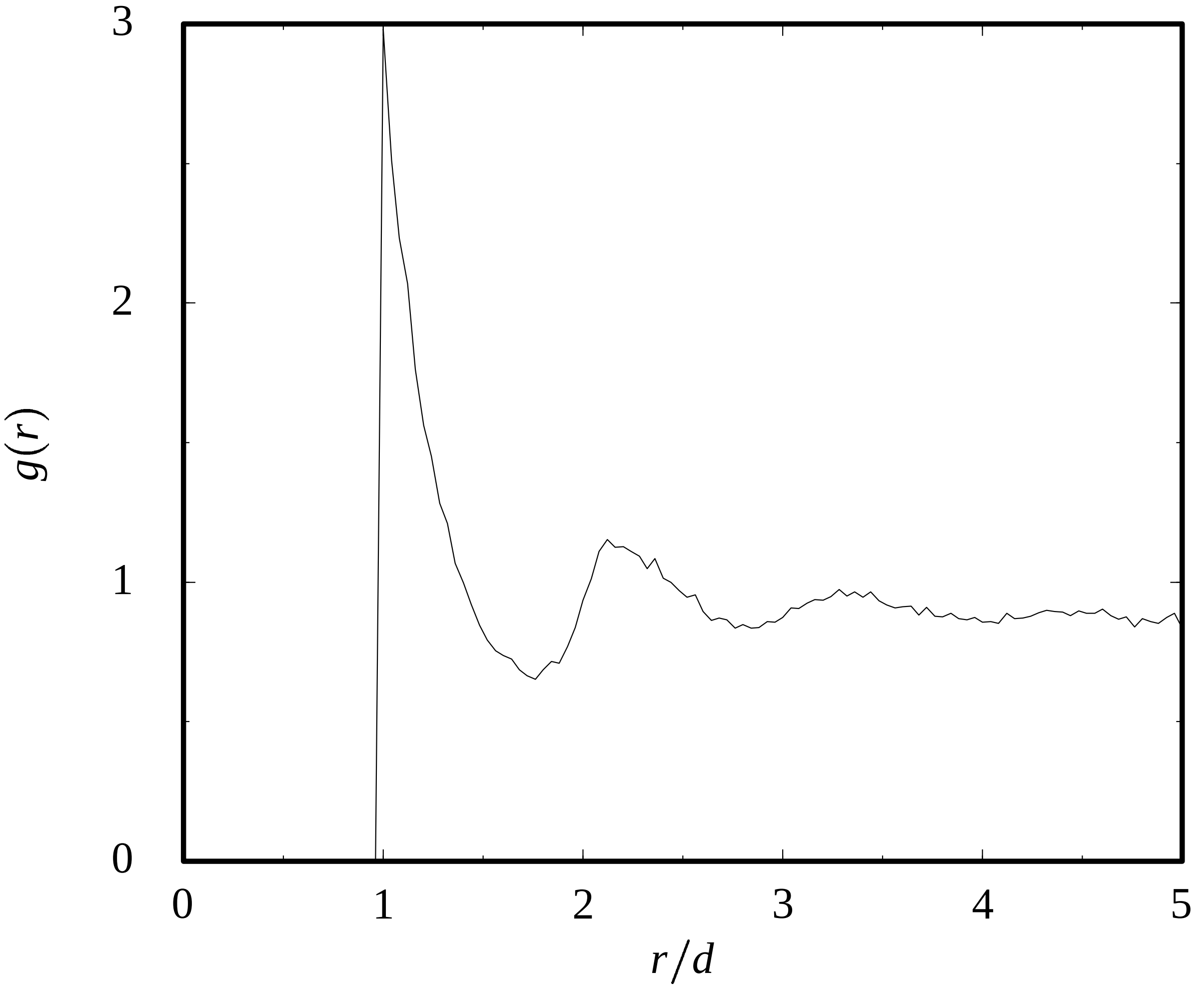
Incoming radiation whose energy $\mathcal{E}$ lies above the onset of absorption at $\mathcal{E}_a$. Receiving atom emits an electron of energy $\mathcal{E} - \mathcal{E}_a$ and wave vector $\hbar k = \sqrt{2m(\mathcal{E} - \mathcal{E}_a)}$.

$$\alpha(\mathcal{E}) \propto \sum_j |1 + [e^{-R_j/l_T} e^{ikR_j} f/R_j]^2|^2 \qquad \text{(L27)}$$

$$\sim \left\langle \int ds\, g(s) e^{-2s/l_T} \cos(2ks) \right\rangle . \qquad \text{(L28)}$$

l_T is the mean free path of electrons in the solid.

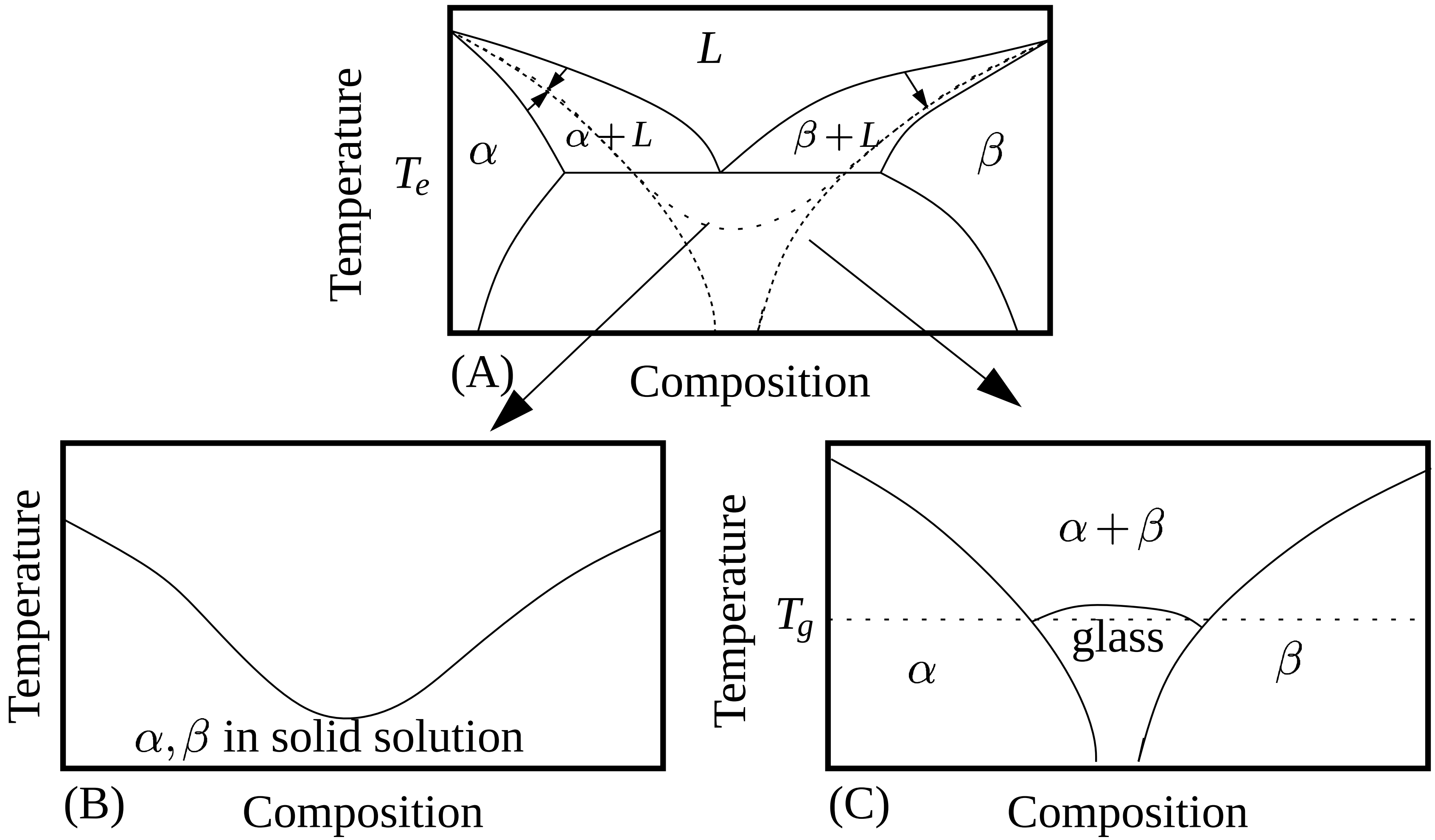
Dense Random Packing, Bernal model, Hard spheres



The radial distribution function $g(r)$ for hard spheres (disks) of radius d in two dimensions.

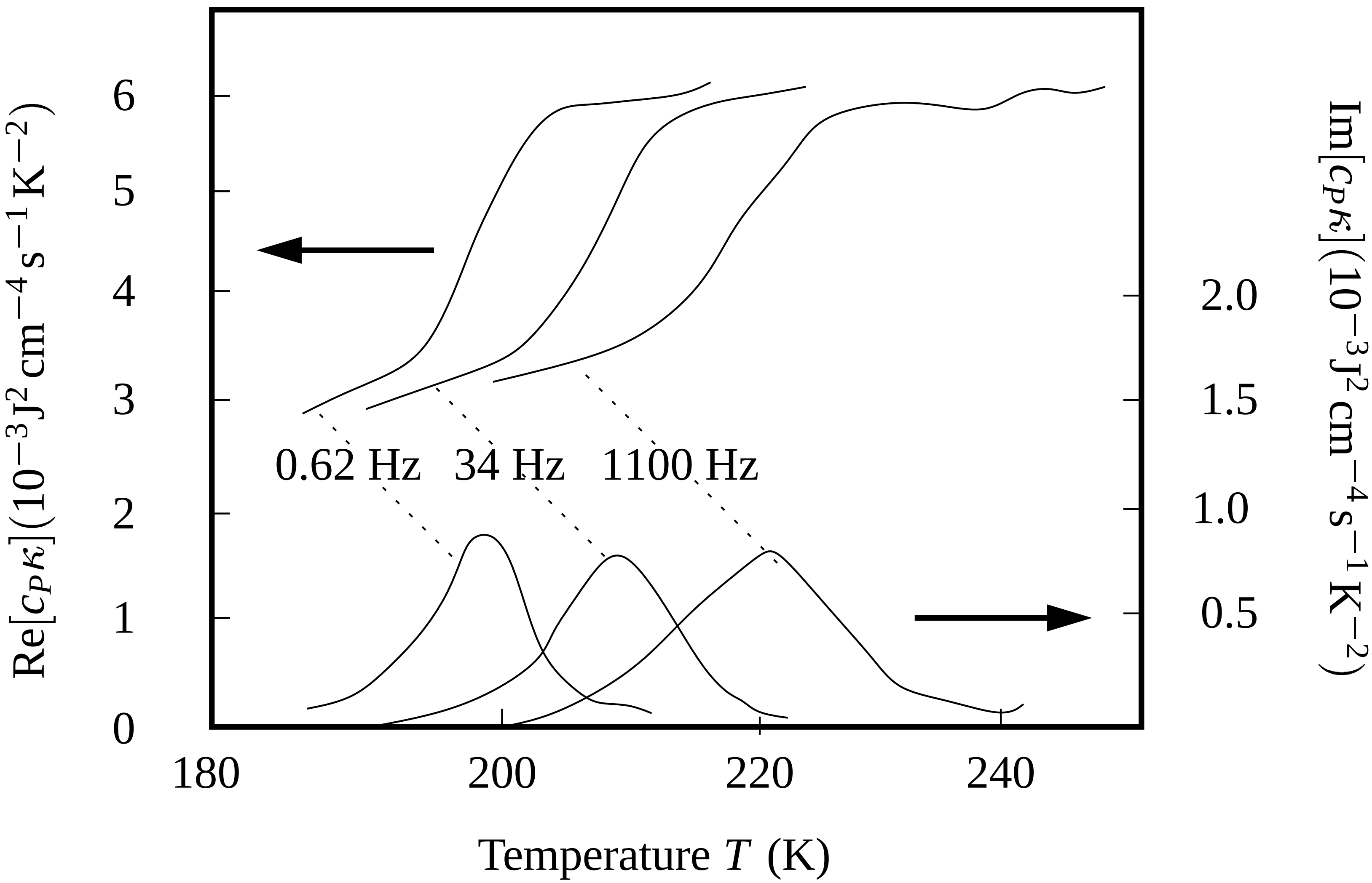
Glasses

$$\eta \propto \exp\left[C/(T - T_0)\right]. \tag{L29}$$



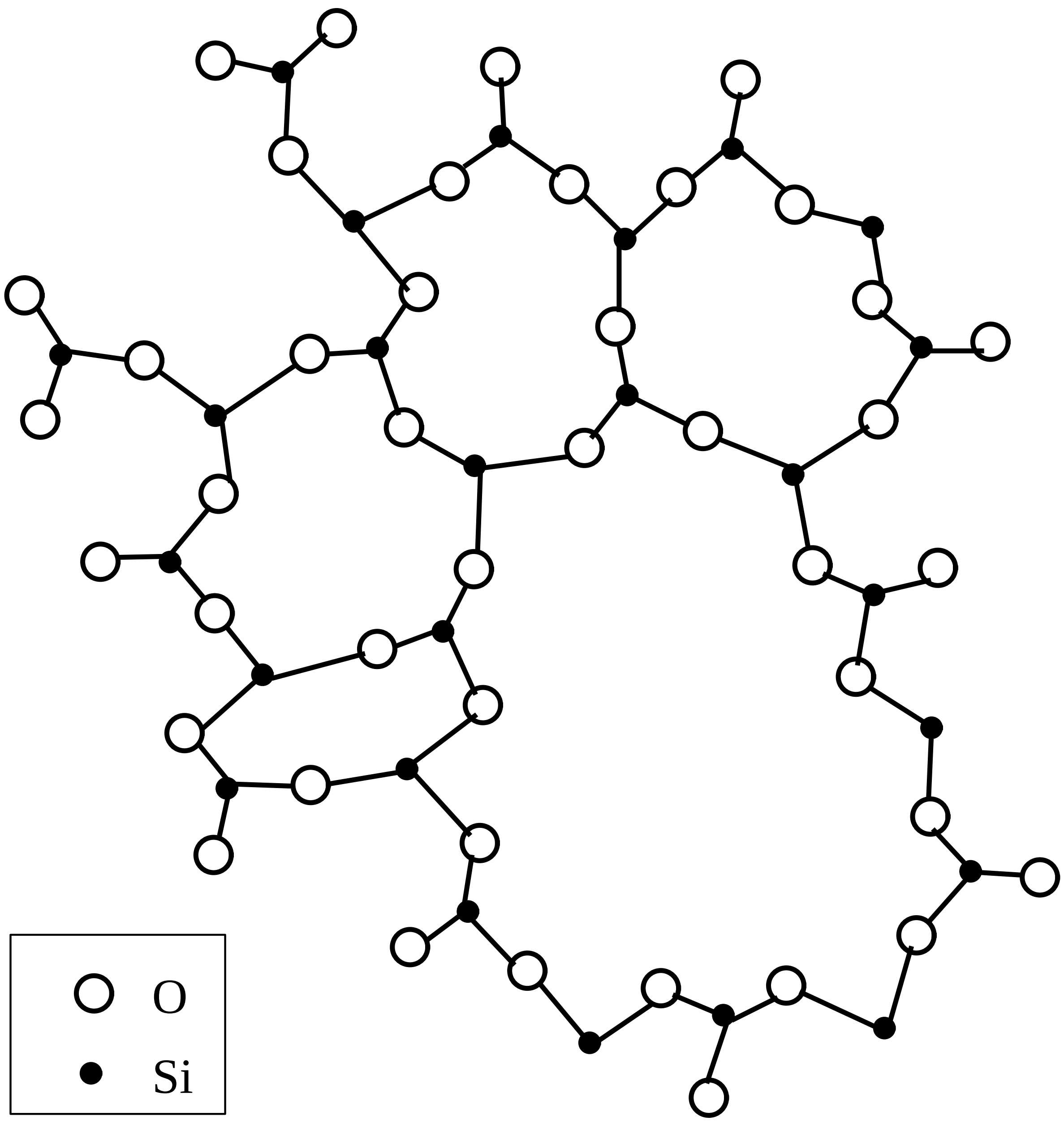
Properties depend upon time one waits.

Glasses



Specifi c heat c_p times thermal conductivity κ for the glassy liquid glycerol as a function of temperature. Birge and Nagel (1985)

Continuous Random Network



Bond-counting and constraint argument of Phillips

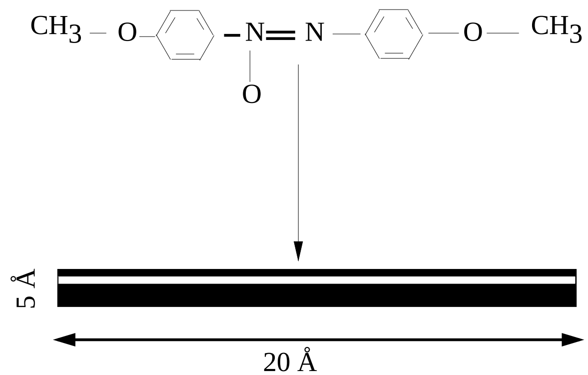
N number of atoms, b number of bonds per atom.

$Nb/2$ total bonds. If there is an optimal angle, $N(2b-3)$ extra constraints per atom.

$$3N = N(2b-3) + \frac{Nb}{2}, \tag{L30}$$

it follows that

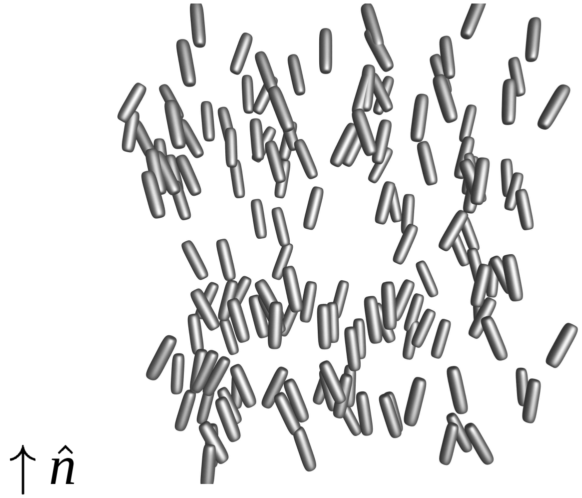
$$b = 2.4, \tag{L31}$$



Picture of the organic molecule p-azoxyanisole (PAA), which forms a nematic liquid crystal between 116 °C and 135 °C. It can roughly be regarded as a rigid rod of length 20 Å and width 5 Å.

- Nematics
- Cholesterics
- Smectics

Liquid Crystals



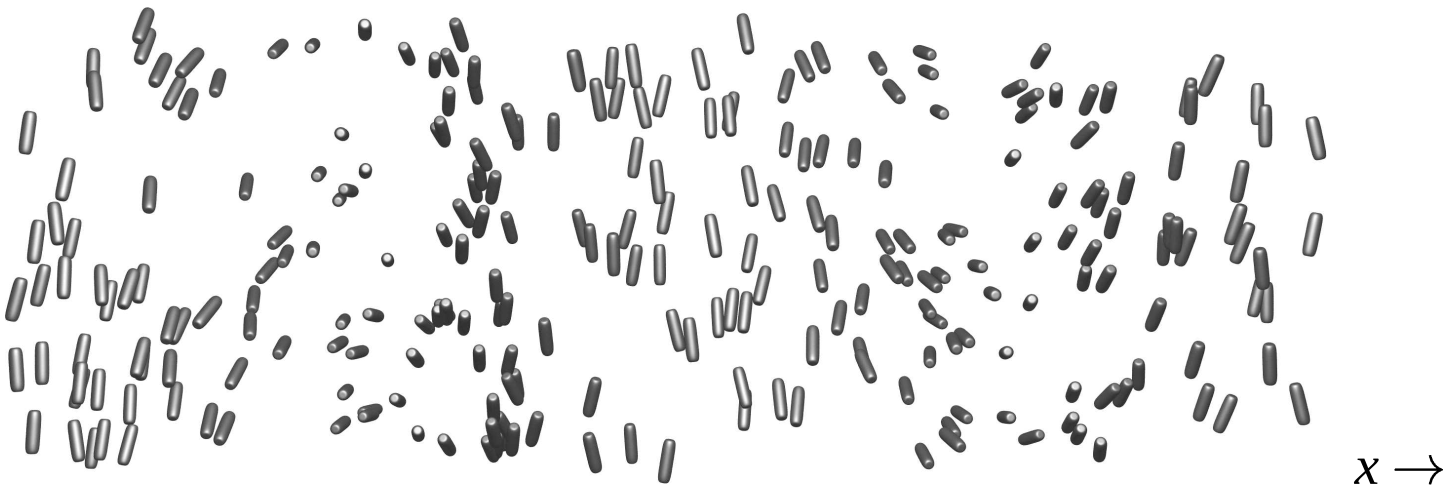
Nematic liquid crystal

Cholesterics

$$n_x = 0 \tag{L32a}$$

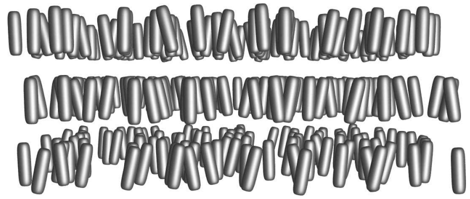
$$n_y = \cos q_0 x \tag{L32b}$$

$$n_z = \sin q_0 x. \tag{L32c}$$



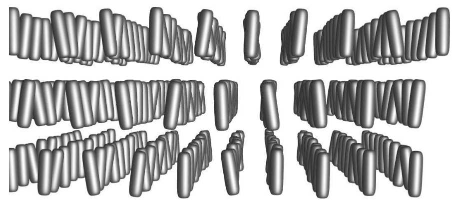
Smectics

Smectic A

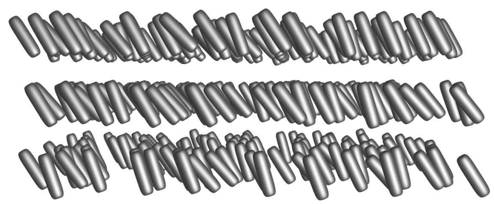


$\uparrow \hat{n}$

Smectic B



Smectic C



$$\mathcal{O} = \int d^3r_1 d\theta_1 n_1(\vec{r}_1, \theta_1) \frac{1}{2}(3\cos^2\theta_1 - 1). \tag{L33}$$

$$Q_{\alpha\beta} = \epsilon_{\alpha\beta} - \frac{1}{3}\delta_{\alpha\beta}\sum_{\gamma}\epsilon_{\gamma\gamma}, \tag{L34}$$

Polymer as a random walk.

Ideal Radius of Gyration

$$\mathcal{P}_{N+1}(\vec{R}) = \int d\vec{R}' \mathcal{P}_N(\vec{R}')\mathcal{P}_1(\vec{R}-\vec{R}') \tag{L35}$$

$$\Rightarrow \quad \mathcal{P}_{N+1}(\vec{k}) = \mathcal{P}_N(\vec{k})\mathcal{P}_1(\vec{k}) \tag{L36}$$

$$\Rightarrow \quad \mathcal{P}_N(\vec{k}) = [\mathcal{P}_1(\vec{k})]^N. \tag{L37}$$

$$\int d\vec{R} \qquad \mathcal{P}_1(\vec{R}) = 1 \Rightarrow \mathcal{P}_1(\vec{k}=0) = 1. \tag{L38}$$

$$\mathcal{P}_1(\vec{k}) \approx 1 - \frac{c}{2}k^2 \approx e^{-ck^2/2} \quad \text{(L39)}$$

$$\Rightarrow \qquad \mathcal{P}_N(\vec{k}) \approx e^{-Nck^2/2} \quad \text{(L40)}$$

$$\Rightarrow \qquad \mathcal{P}_N(\vec{R}) = \frac{1}{\sqrt{2\pi Nc}^3} e^{-R^2/2Nc}. \quad \text{(L41)}$$

Central limit theorem

$$c = -\frac{\partial^2}{\partial k^2}|_{\vec{k}=0} \mathcal{P}_1(\vec{k}) = \int d\vec{R}\, R^2 \mathcal{P}_1(\vec{R}) \equiv a^2 \quad \text{(L42)}$$

$$\mathcal{R}_I{}^2 \quad = \quad \int d\vec{R}\, R^2 \mathcal{P}_N(\vec{R}) = 3cN = 3a^2 N \quad \text{(L43)}$$

$$\Rightarrow \mathcal{R}_I \quad = \quad a\sqrt{3N}. \quad \text{(L44)}$$

$$S = S_0 - \frac{3}{2} k_B \frac{R^2}{\mathcal{R}_I{}^2} \quad \text{(L45)}$$

$$\mathcal{F} = \mathcal{F}_0 + \frac{3}{2} k_B T \frac{R^2}{\mathcal{R}_\mathrm{I}{}^2} = \mathcal{F}_0 + \frac{1}{2} k_B T \frac{R^2}{a^2 N}, \tag{L46}$$

$$\vec{F} = 3 k_B T \frac{\vec{R}}{\mathcal{R}_\mathrm{I}{}^2} = \frac{k_B T}{a^2 N} \vec{R} \equiv \frac{\mathcal{K}}{N} \vec{R}. \tag{L47}$$

Polymer behaves like an ideal spring

Spring constant that rises in proportion to temperature, falls in proportion to the molecular weight $\mathcal{R}_\mathrm{I}{}^2 \propto N$

$$M \sim \frac{\mathcal{R}^2}{a^2} \tag{L48}$$

$$\mathcal{F} = \mathcal{F}_0 + k_B T \left(\frac{N}{M}\right) \frac{1}{2} \frac{\mathcal{R}^2}{a^2 M} = \mathcal{F}_0 + k_B T \frac{N}{2} \frac{a^2}{\mathcal{R}^2} = \mathcal{F}_0 + k_B T \frac{\mathcal{R}_\mathrm{I}^2}{6 \mathcal{R}^2}. \tag{L49}$$

$$P = -\frac{\partial}{\partial \mathcal{R}^3} k_B T N \frac{a^2}{\mathcal{R}^2} \propto \frac{k_B T (N/M)}{\mathcal{R}^3}, \tag{L50}$$

Pressure of an ideal gas of N/M particles in volume $\mathcal{R}^3$.

$$n = \frac{N}{\mathcal{R}^3} = \frac{\mathcal{R}_{\mathrm{I}}^2}{a^2\mathcal{R}^3}. \tag{L51}$$

$$\mathcal{F} \propto k_B T \mathcal{R}^3 [An + Bn^2 + Cn^3 + \ldots]. \tag{L52}$$

$$\mathcal{F} = \mathcal{F}_0 + k_B T \left[\frac{\mathcal{R}^2}{{\mathcal{R}_{\mathrm{I}}}^2} + \frac{\mathcal{R}_{\mathrm{I}}^2}{\mathcal{R}^2} + \mathcal{R}^3 \left[A\left(\frac{\mathcal{R}_{\mathrm{I}}^2}{a^2\mathcal{R}^3}\right) + B\left(\frac{\mathcal{R}_{\mathrm{I}}^2}{a^2\mathcal{R}^3}\right)^2 + C\left(\frac{\mathcal{R}_{\mathrm{I}}^2}{a^2\mathcal{R}^3}\right)^3 + \ldots\right]\right]. \tag{L53}$$

$$2\frac{\mathcal{R}}{\mathcal{R}_{\mathrm{I}}^2} - 2\frac{\mathcal{R}_{\mathrm{I}}^2}{\mathcal{R}^3} - 3B\frac{\mathcal{R}_{\mathrm{I}}^4}{a^4\mathcal{R}^4} - 6C\frac{\mathcal{R}_{\mathrm{I}}^6}{a^6\mathcal{R}^7} = 0. \tag{L54}$$

$$2\frac{\mathcal{R}}{\mathcal{R}_{\mathrm{I}}^2} - 3B\frac{\mathcal{R}_{\mathrm{I}}^4}{a^4\mathcal{R}^4} = 0 \tag{L55}$$

$$\Rightarrow \quad \mathcal{R}^5 \propto \frac{B\mathcal{R}_{\mathrm{I}}^6}{a^4} \Rightarrow \mathcal{R} \propto \mathcal{R}_{\mathrm{I}}^{6/5} \propto N^{3/5}. \tag{L56}$$

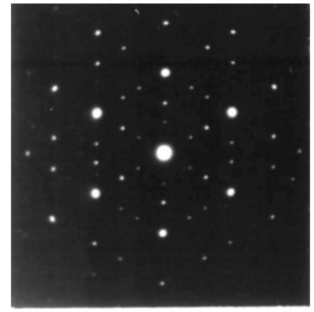
$$\frac{|B|\mathcal{R}_{\mathrm{I}}^4}{a^4\mathcal{R}^4} = 2C\frac{\mathcal{R}_{\mathrm{I}}^6}{a^6\mathcal{R}^7} \Rightarrow \mathcal{R}^3 \sim \frac{C\mathcal{R}_{\mathrm{I}}^2}{|B|a^2} \sim N \Rightarrow \mathcal{R} \sim N^{1/3}. \tag{L57}$$

Θ solvent

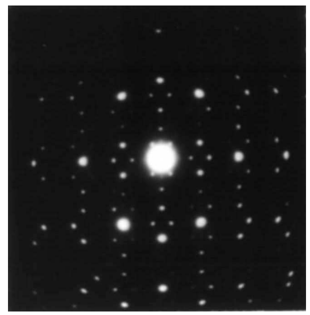
Quasicrystals

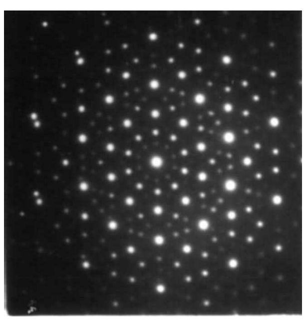
Five–fold symmetry is impossible... and yet

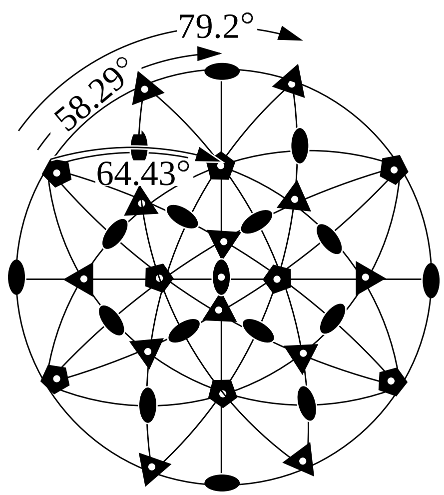
79.2°



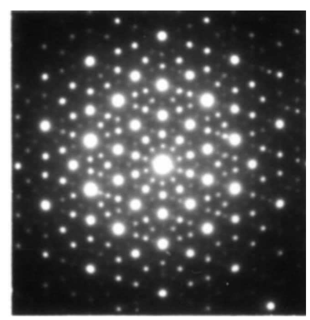
58.29°

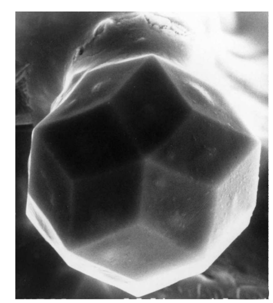






64.43°





Shechtman et al. (1984) Quasi-crystal site with several applets

$$x_n = n + (\tau - 1)\mathrm{int}(n/\tau). \tag{L58}$$

Golden Mean

$$\tau = 1 + \frac{1}{\tau} = \frac{\sqrt{5}+1}{2} = 1.618\ldots, \tag{L59}$$

Deflation rule:

Replace τ with sequence $\tau, 1$,

Replaces every 1 with a τ

$$\tau 1 \tau \tau 1 \ldots. \tag{L60}$$

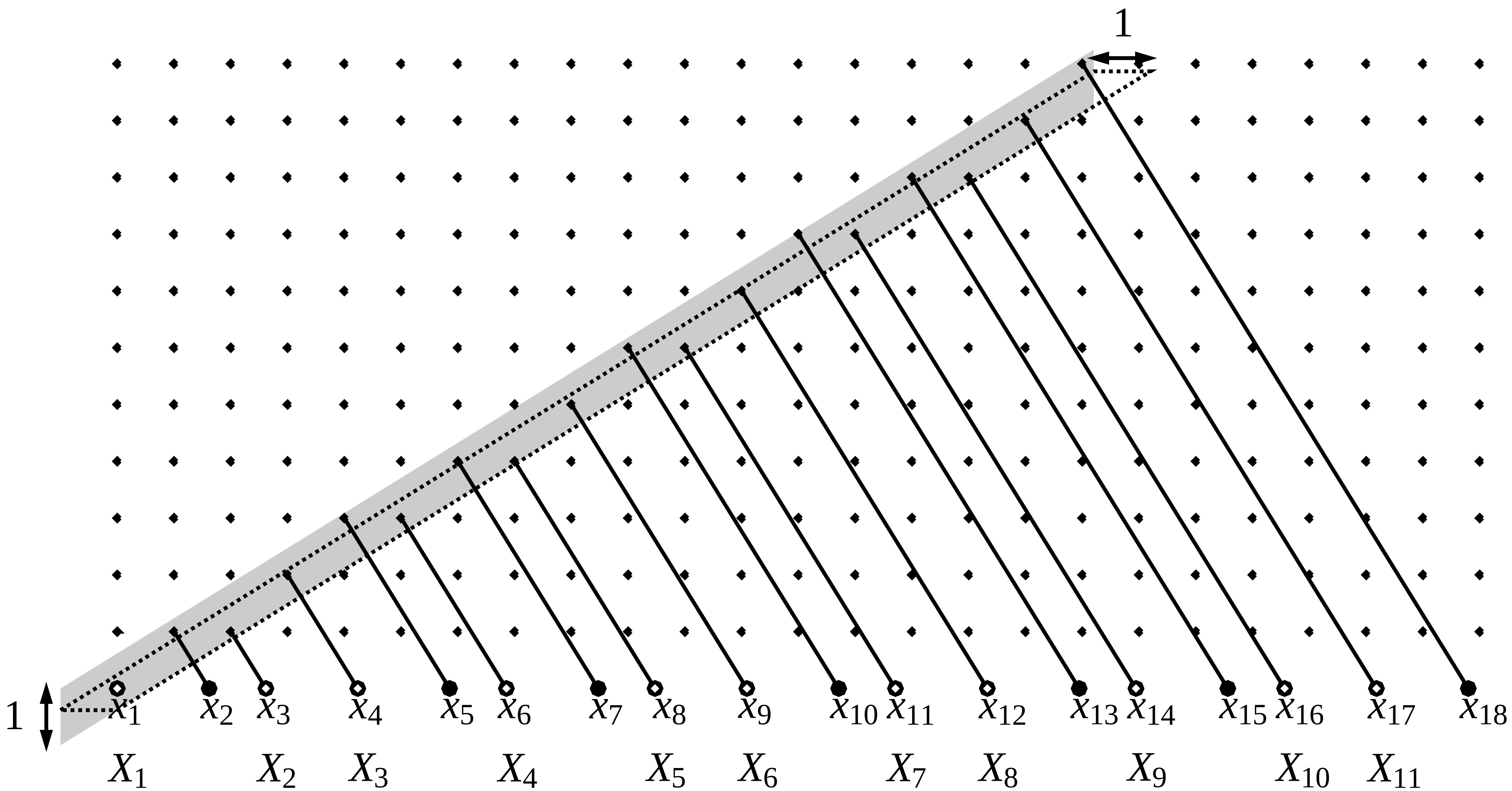
$$\tau 1 \tau \tau 1 \tau 1 \tau \ldots. \tag{L61}$$

$$X_{n+1} = X_n X_{n-1}, \tag{L62}$$

One-Dimensional Quasicrystal

$$X_{-1} = \tau; X_0 = \tau 1; X_1 = \tau 1 \tau; X_2 = \tau 1 \tau \tau 1 \ldots \quad \text{(L63)}$$

$$X_3 = X_2 X_1 = \tau 1 \tau \tau 1 \tau 1 \tau. \quad \text{(L64)}$$



One-Dimensional Quasicrystal

$$x_m = m + \sum_n n\theta(n - m/\tau + 1)\theta(m/\tau - n)/\tau \tag{L65}$$

$$x/\tau > y > x/\tau - 1. \tag{L66}$$

$$[m, \sum_n n\theta(m/\tau - n)\theta(n - [m/\tau - 1])]. \tag{L67}$$

$$(x+1)/\tau - 1 > y > x/\tau - 1. \tag{L68}$$

$$[\sum_m m\theta((m+1)/\tau - 1 - n)\theta(n - [m/\tau - 1]), n]. \tag{L69}$$

$$X_{n+1} = \sum_m m\theta((m+1)/\tau - n - 1)\theta(n - m/\tau + 1) + n/\tau. \tag{L70}$$

X_n hollow circles. , $X_m = -1/\tau + \tau x_m$.

Scattering from a One-Dimensional Quasicrystal

$$\Sigma_q = \sum_n e^{iqx_n} \tag{L71}$$

$$= \sum_{n,m} e^{iq(m+n/\tau)}\theta(n-m/\tau+1)\theta(m/\tau-n) \tag{L72}$$

$$= \int dxdy\, e^{i\vec{q}\cdot(x,y)} \left[\sum_{m,n} \delta(x-m)\delta(y-n)\right] \theta(y-x/\tau+1)\theta(x/\tau-y) \tag{L73}$$

$$\text{where } \vec{q} = (q, q/\tau). \tag{L74}$$

First piece

$$A(\vec{q}) = \int dxdy \sum_{m,n} \delta(x-m)\delta(y-n) e^{iq_x x} e^{iq_y y} \tag{L75}$$

$$= N\frac{(2\pi)^2}{\mathcal{V}} \sum_{n',m'} \delta(q_x - 2\pi n')\delta(q_y - 2\pi m'). \tag{L76}$$

Second piece

$$B(\vec{q}) = \int dx \int_{x/\tau-1}^{x/\tau} dy\, e^{iq_x x + iq_y y} = \int dx\, e^{iq_x x} \left[\frac{e^{iq_y(x/\tau)} - e^{iq_y(x/\tau-1)}}{iq_y} \right]. \quad \text{(L77)}$$

$$\Sigma_q \propto$$

$$\int dx dq'_x dq'_y \sum_{n',m'} \left\{ \begin{array}{c} \delta(q - q'_x - 2\pi n') \\ \times \delta(q/\tau - q'_y - 2\pi m') \end{array} \right\} \left[\frac{e^{iq'_y(x/\tau)} - e^{iq'_y(x/\tau-1)}}{iq'_y} \right] e^{iq'_x x} \quad \text{(L78)}$$

$$= \int dx \sum_{n',m'} \left[\frac{e^{i(q/\tau-2\pi m')(x/\tau)} - e^{i(q/\tau-2\pi m')(x/\tau-1)}}{iq/\tau - 2\pi i m'} \right] e^{i(q-2\pi n')x} \quad \text{(L79)}$$

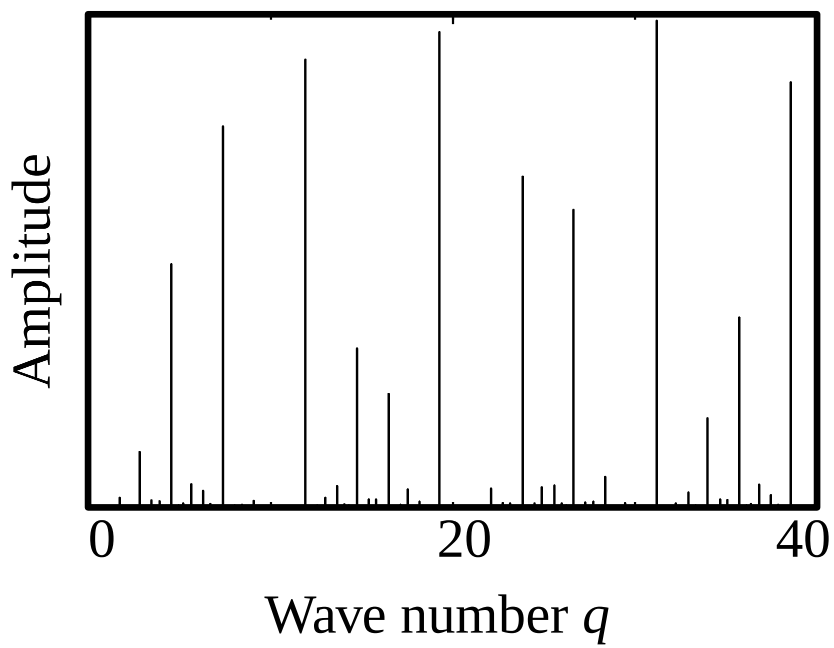
$$= 2\pi \sum_{n',m'} \frac{1 - e^{-i(q/\tau-2\pi m')}}{iq/\tau - 2\pi i m'} \delta([2\pi m' - \frac{q}{\tau}]/\tau + 2\pi n' - q). \quad \text{(L80)}$$

The peaks of (80) are at

$$\frac{2\pi(m'/\tau + n')}{\tau^{-2} + 1} = q \quad \text{(L81)}$$

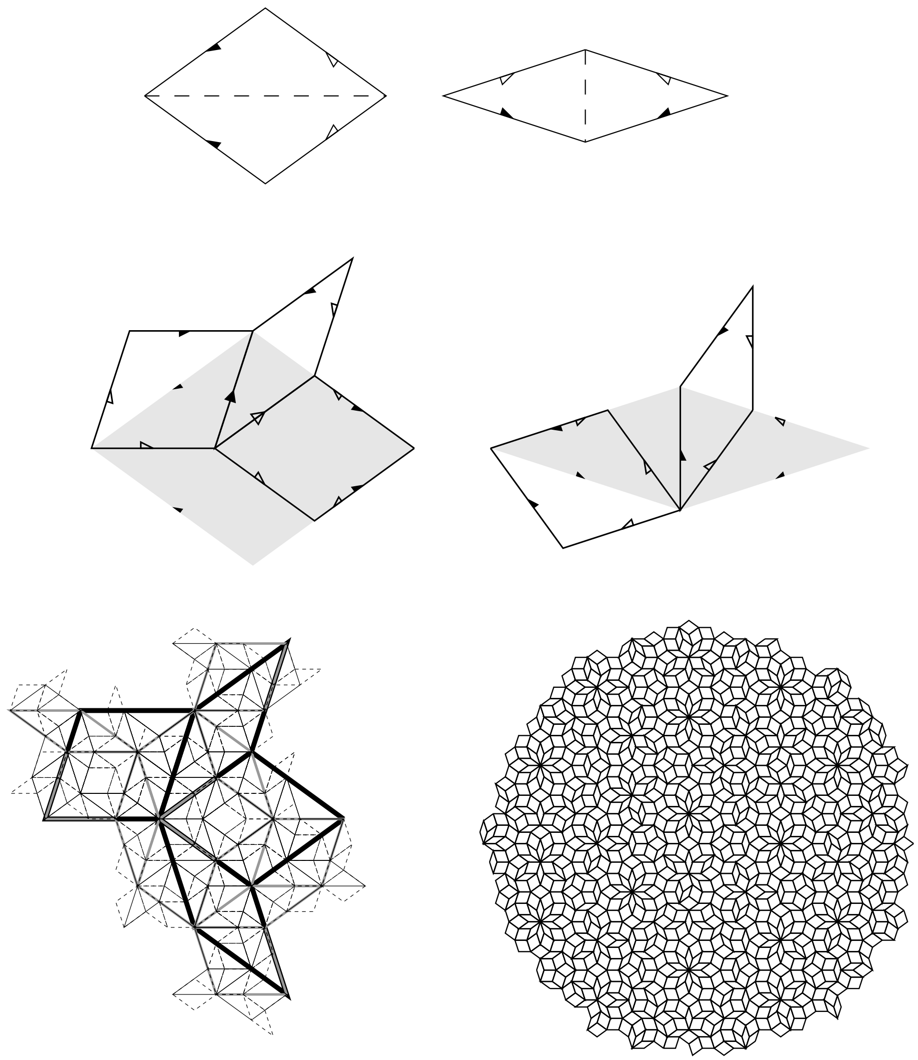
Square amplitude is proportional to

$$\sin^2\left(\pi\left[\frac{m'\tau - n'}{\tau+\tau^{-1}}\right]\right) / \left(q/\tau - 2\pi m'\right)^2 . \tag{L82}$$

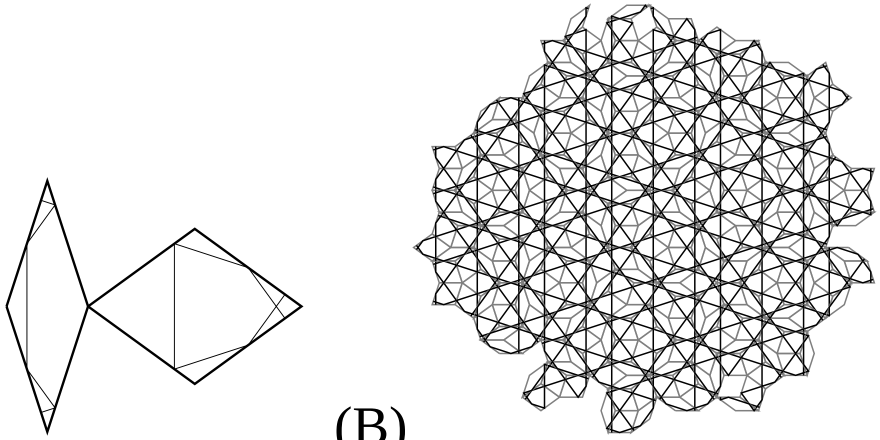


Two-Dimensional Quasicrystals—Penrose Tiles

Penrose, Gardner



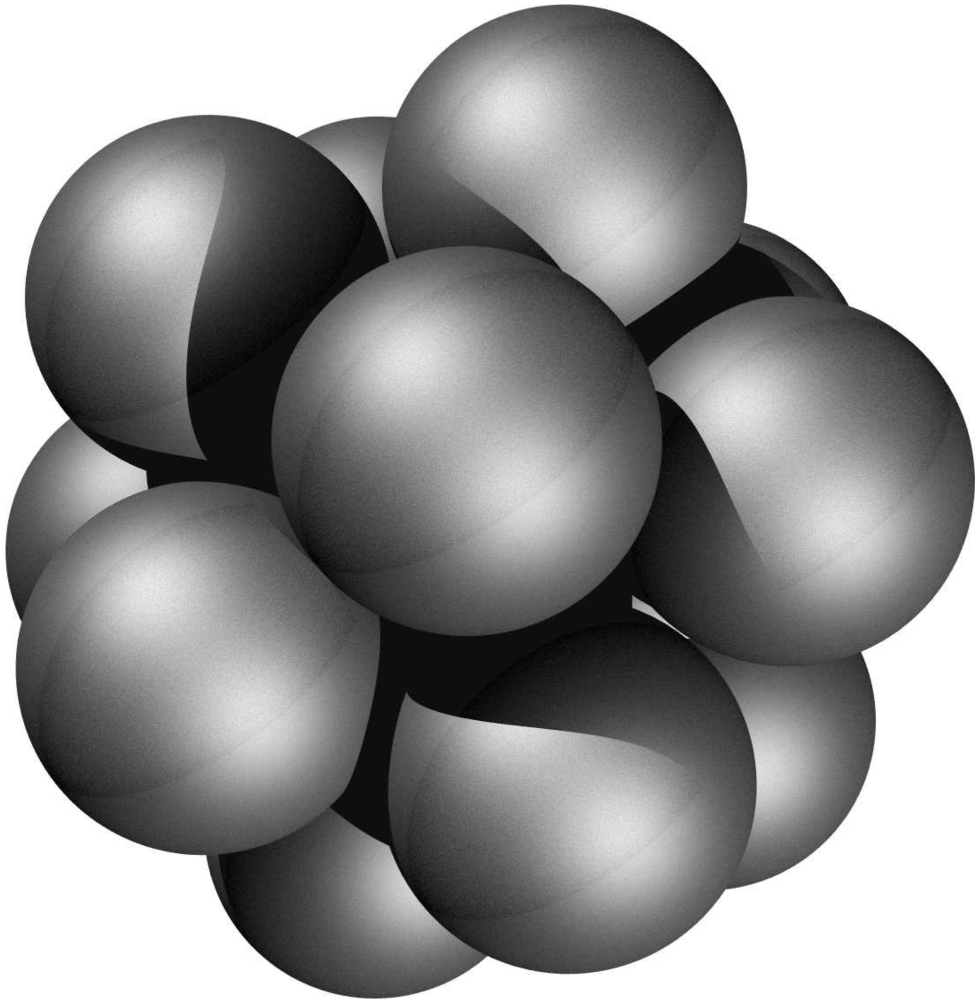
Amman lines



(A) (B)

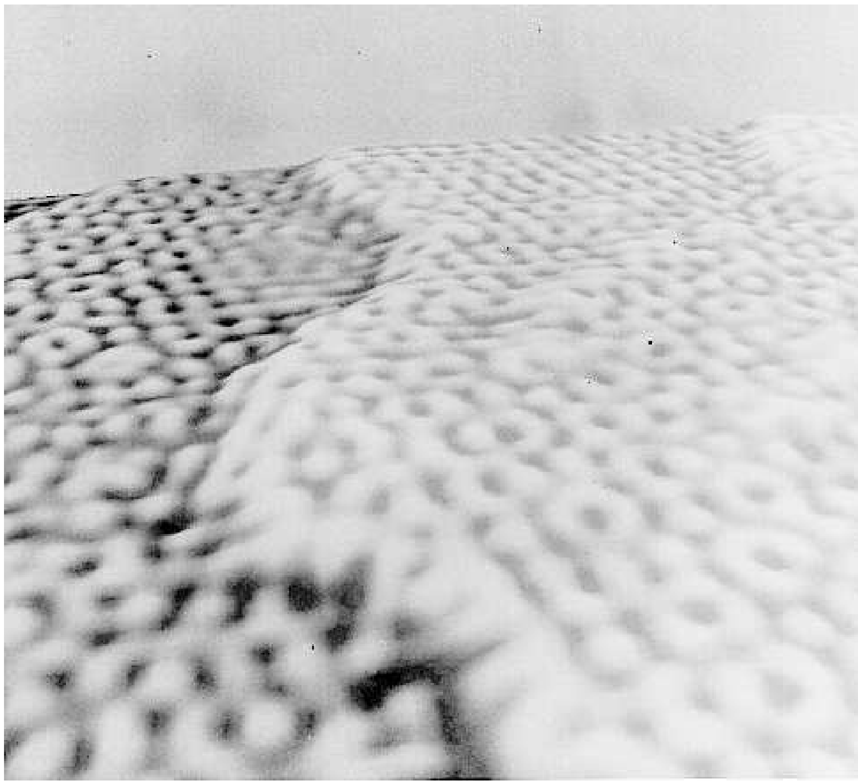
$$\vec{r}\cdot\hat{e}_\alpha = x_{n_\alpha},\ \vec{r}\cdot\hat{e}_\beta = x_{n_\beta}, \tag{L83}$$

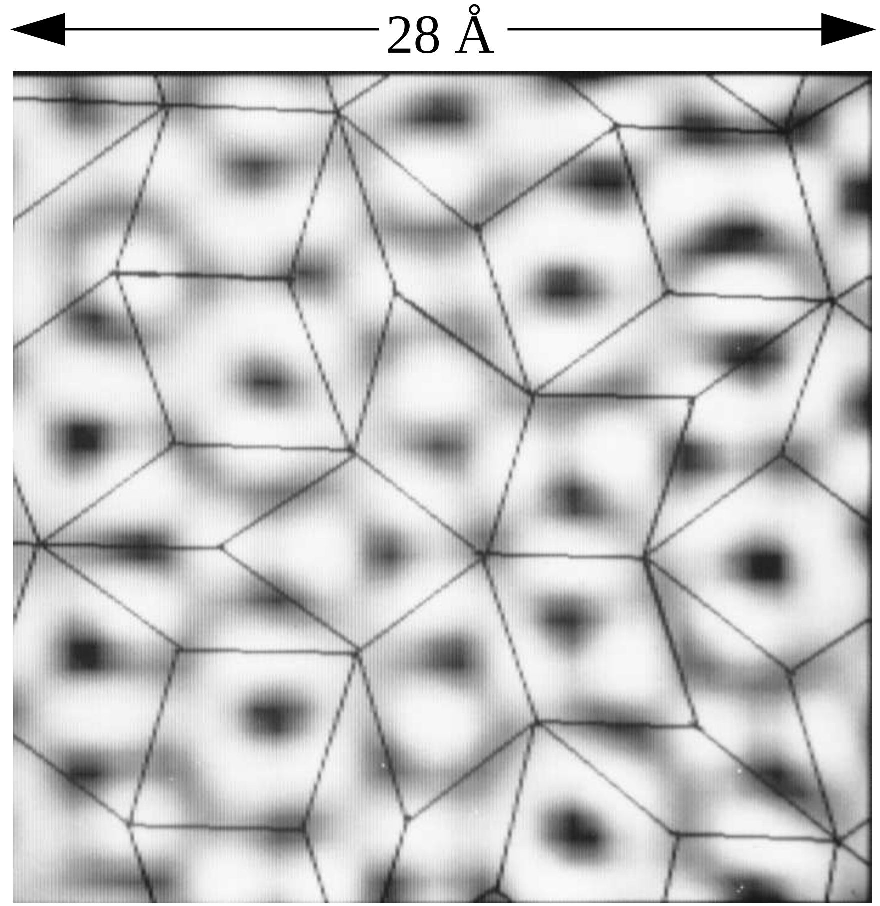
Physical reasons for quasicrystals



Al_6Li_3Cu is real equilibrium quasicrystal

Physical reasons for quasicrystals

(A) 

(B) 

Kortan (1996)

David Tomanek's Nanotube Site