

CONFIGURATIONAL THERMODYNAMICS

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BASIC IDEAS OF STATISTICAL THERMODYNAMICS

Objects: systems composed of **many** particles

Natural application:

macroscopic bodies composed of $N \propto 10^{23}$ atoms/molecules

Basic notions:

- **Microscopic state of a macroscopic body:** a state given by **particular** states of all atoms/molecules
- **Macroscopic state of a macroscopic body:** a state **directly observed** (shape, hardness, roughness, colour etc.)

Basic parameters and functions:

- **Internal energy:** sum of all types of energies of atoms/molecules building a macroscopic body. *Internal energy is highly degenerated with respect to microscopic states of the body.*
- **Temperature:** parameter, whose value is equal in bodies being in thermal equilibrium

Interpretation of temperature:

a quantity T proportional to an average **kinetic** energy of **one** atom/molecule - a measure of **chaotic** motion of atoms/molecules

Factors controlling the generation of a concrete macroscopic state of a macroscopic body:

- (I) Tendency for attaining possibly **lowest value of internal energy E** ,
- (II) Probability for reaching such energy – **number p of microscopic states** corresponding to this energy. **p increases with increasing energy**

Importance of the factor (II) increases with increasing temperature

CONSEQUENCE:

The **observed equilibrium** macroscopic state is a compromise between both factors.

Quantitatively it corresponds to a minimum value of a function

$$F = E - T \times k_B \times \ln(p), \quad k_B = \text{const.} \quad \leftarrow \text{free energy}$$

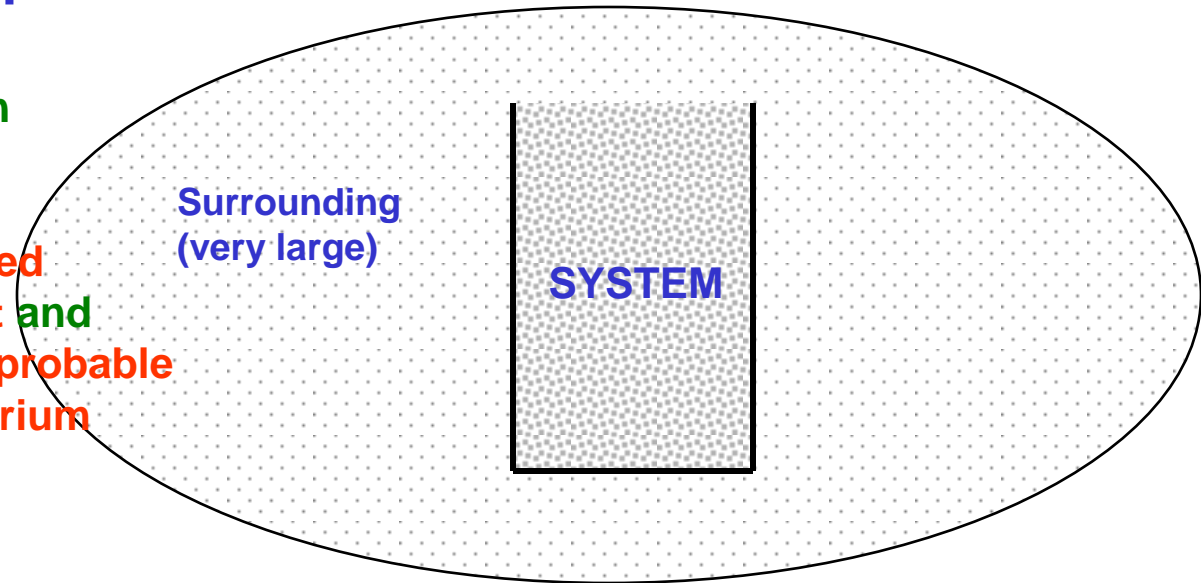
More rigorous approach:

Entropy: $S = k_B \times \ln(p)$ - defined for an equilibrium state !!!!

Relation between S and T : $T = \left[\frac{\partial S}{\partial E} \right]^{-1}$

STANDARD ASSUMPTIONS:

- The system is much smaller than the surrounding
- The **whole supersystem** (system + surrounding) is **isolated** - hence its energy E_0 is **constant** and all microscopic states are **equiprobable**
- The system is in **thermal equilibrium** with the surrounding - hence its temperature equals T_0



Question:

What is the probability $P(Q)$ that the system is in a microscopic state Q with the internal energy $E(Q)$?

NOTE ! The question makes sense, because the **system is not isolated !!**

p – number of possible microstates of the **supersystem**, for which the system is in the microstate Q

$$P(Q) \propto p$$

Entropy S_0 of the **surrounding**:

$$S_0(Q) = k_B \times \ln(p) \Rightarrow P(Q) \propto \exp\left[\frac{S_0(Q)}{k_B}\right]$$

But: $S_0(Q) \equiv S_0[E_0 - E(Q)] \approx S_0(E_0) - \frac{\partial S_0}{\partial E_0} \times E(Q) + \dots$

$$S_0(Q) \approx S_0(E_0) - \frac{E(Q)}{T}$$

and thus:

$$P(Q) = \frac{\exp\left[-\frac{E(Q)}{k_B T}\right]}{Z} \quad \text{where} \quad Z = \sum_Q \exp\left[-\frac{E(Q)}{k_B T}\right] \quad \leftarrow \text{partition function}$$

It is proved that:

$$F = -k_B T \times \ln(Z)$$

Thermodynamics of solid solutions

Solid solution:

A solid multicomponent phase existing for a finite range of the component concentrations.

Configurational free energy of a solid solution: part of the free energy which depends exclusively on the configuration of atoms over the crystalline lattice



$$\frac{1}{N} \times F = f = c \times f_A + (1-c) \times f_B$$



$$f = c \times f_A + (1-c) \times f_B + \Delta f$$

$$\Delta f = \Delta u - T \times \Delta s$$

configurational
free energy of mixing

configurational
internal energy of mixing

configurational
entropy of mixing

THEORETICAL JUSTIFICATION FOR THE SEPARATION OF NON-CONFIGURATIONAL TERMS OF THE FREE ENERGY:

The term “chemical order” is connected with atomic configuration; i.e. with an arrangement of atoms over the sites of a crystalline lattice. As recently formulated,⁽¹⁾ two very different time scales exist in a real crystal: a slow one for atomic interchanges (creating configurations) and a much faster one for lattice vibrations and electronic motions. Consequently, it is possible to perform statistical averages separately over these types of process (for references to original papers see Ref. 1). It is then assumed that only “one-way” coupling exists between the particular energy terms:

$$E_{\text{tot}}(\text{state}) = E_c(\sigma) + E_{\text{oth}}(\sigma) \quad (1)$$

where:

- σ atomic configuration,
- $E_{\text{tot}}(\text{state})$ total crystal energy attributed to a particular state,
- $E_c(\sigma)$ configurational energy and
- $E_{\text{oth}}(\sigma)$ energy of other degrees of freedom (vibrations, electronic motions) which are dependent, however, on the configuration.

The partition function is thus given by:

$$Z = \sum_{\{\sigma\}} \exp \left[- \frac{\Psi(\sigma)}{kT} \right] \quad (2)$$

where:

$$\Psi(\sigma) = E_c(\sigma) + E_{\text{oth}}(\sigma) - T \times S_{\text{oth}}(\sigma) \quad (3)$$

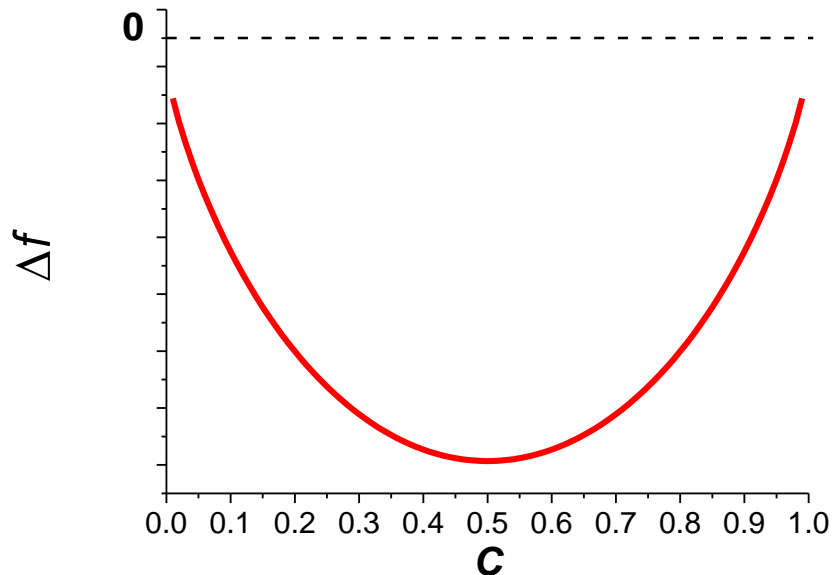
and $S_{\text{oth}}(\sigma)$ represents a set of configuration-dependent functionals of entropies connected with other degrees of freedom.

IDEAL SOLUTION

$$\Delta u = 0 \Rightarrow \Delta f = T \times \Delta s, \quad \Delta s = k_B \times \ln W$$

W – number of distinct configurations of A and B atoms over the crystalline lattice of the solid solution

$$W = \frac{N!}{(cN)! \times [(1-c)N]!}; \quad \ln W \approx -N[c \ln c + (1-c) \ln(1-c)] \quad \text{valid for large } N$$



REGULAR SOLUTION

$$\Delta u \neq 0$$

$$\Delta u = u_{sol} - u_0$$

internal energy of a solution

internal energy of not-mixed elements

THERMODYNAMICS:

$$F = -k_B \times T \times \ln Z \quad Z = \sum_{all \text{ states}} \exp\left[-\frac{E(state)}{k_B T}\right]$$

$$E(state) = E_{conf} + E_{other}(conf)$$

configurational energy

energy of other degrees of freedom related to particular configuration

COMMENT:

Such grouping of energies is reasonable due to different time scales (mentioned earlier)

Consequence:

$$Z = \sum_{conf} \exp\left[-\frac{E_{conf}}{k_B T}\right] \times \left\{ \sum_{other(conf)} \exp\left[-\frac{E_{other}(conf)}{k_B T}\right] \right\} \exp\left[-\frac{F_{other}(conf)}{k_B T}\right]$$

The partition function Z may thus be written down as:

$$Z = \sum_{conf} \left\{ \exp \left[- \frac{E_{conf} + F_{other}(conf)}{k_B T} \right] \right\}$$

where

$$E_{conf} + F_{other}(conf) = \bar{E}_{conf} \leftarrow \text{“average” configurational energy accounting for averaging over non-configurational degrees of freedom assigned to a particular configuration}$$

Modelling of the (average) configurational energy

First approximation: pair-interactions of nearest-neighbouring (nn) atoms
– the Ising model:

$$\bar{E}_{conf} = \sum_{i,j} (N_{ij} \times V_{ij})$$

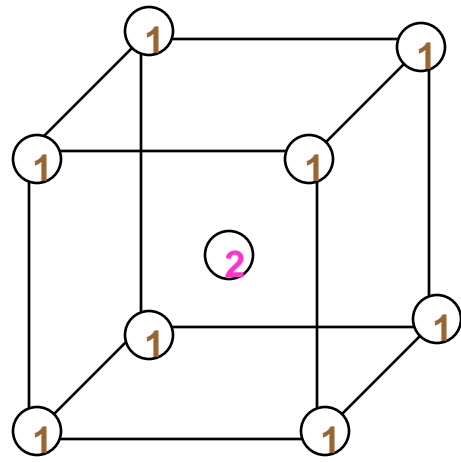
,where N_{ij} is a number of i-j nn pairs,
 V_{ij} is the i-j nn pair interaction energy

TWO-COMPONENT (BINARY) A-B SYSTEM

Description of the atomic configuration of the system:

- N** – total number of atoms (both A- and B-type),
- C** – concentration of B-type atoms $C = N_B/N$
- Z** – co-ordination number: number of nn lattice sites surrounding a lattice site; **in bcc structure Z = 8**

$N_A^{(1)}, N_A^{(2)}$ Numbers of A- and B-type atoms occupying 1- and 2-type sublattice sites
 $N_B^{(1)}, N_B^{(2)}$



bcc-type lattice with two sublattices consisting of $N^{(1)}$ and $N^{(2)}$ lattice sites, respectively

Fundamental relationships:

$$\begin{aligned}
 N_A^{(1)} + N_A^{(2)} &= (1-c) \times N \\
 + &+ \\
 N_B^{(1)} + N_B^{(2)} &= c \times N \\
 \parallel &\parallel \\
 \frac{1}{2}N &- \frac{1}{2}N
 \end{aligned}$$



$$\begin{aligned}
 N_A^{(2)} &= (1-c)N - N_A^{(1)} \\
 N_B^{(1)} &= \frac{1}{2}N - N_A^{(1)} \\
 N_B^{(2)} &= \left(c - \frac{1}{2}\right)N + N_A^{(1)}
 \end{aligned}$$

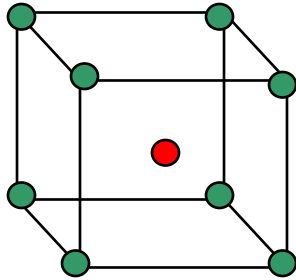
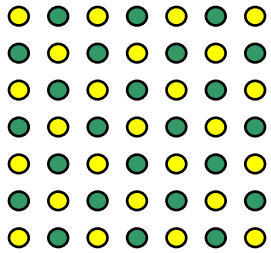
$$\begin{aligned}
 Z \times N_A^{(1)} + Z \times N_A^{(2)} &= 2N_{AA} + N_{AB} = Z \times (1-c) \times N \\
 Z \times N_B^{(1)} + Z \times N_B^{(2)} &= 2N_{BB} + N_{AB} = Z \times c \times N
 \end{aligned}$$



$$\begin{aligned}
 N_{AB} &= Z \times (1-c) \times N - 2N_{AA} \\
 N_{BB} &= Z \times \left(c - \frac{1}{2}\right) \times N + N_{AA}
 \end{aligned}$$

CONCLUSION: $N_A^{(1)}$ and N_{AA} are independent variables !!

ATOMIC (CHEMICAL) ORDER



Long-range order (LRO):

Differentiation „ η ” of probabilities of particular sublattice sites being occupied by particular atoms.

Diffraction: superstructure peaks

Related variables: $N_A^{(1)}$

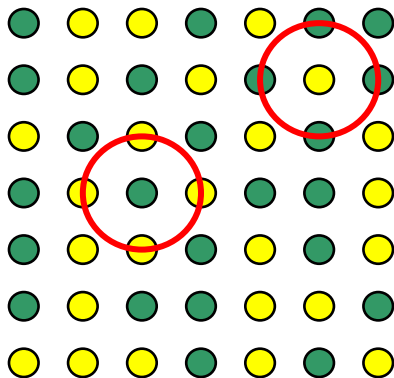
presence of LRO $\frac{N_A^{(1)}}{N^{(1)}} \neq \frac{N_A^{(2)}}{N^{(2)}}; \frac{N_B^{(1)}}{N^{(1)}} \neq \frac{N_B^{(2)}}{N^{(2)}}$

absence of LRO $\frac{N_A^{(1)}}{N^{(1)}} = \frac{N_A^{(2)}}{N^{(2)}}; \frac{N_B^{(1)}}{N^{(1)}} = \frac{N_B^{(2)}}{N^{(2)}}$

LRO parameter:

$$\eta = \frac{p_{A1} + c - 1}{c}; \quad c \leq 1$$

$$p_{A1} = \frac{N_A^{(1)}}{N_1}; \quad 0 \leq \eta \leq 1$$



Short-range order (SRO):

Tendency for A-(B-) atoms to be preferentially surrounded by B- or A-atoms (correlation functions).

Diffraction: diffuse scattering, background modulation between Bragg peaks

Related variables: $P(N_{AA}) = 2N_{AA}/(ZxN)$

SRO parameter: $\alpha = |P(N_{AA}) - (1-c)^2|$

NOTE: η and α are totally independent !

CONFIGURATIONAL ENERGY OF MIXING E_M



$$\bar{E}_{conf} = \sum_{i,j} (N_{ij} \times V_{ij}) = N_{AA} \times V_{AA} + N_{BB} \times V_{BB} + N_{AB} \times V_{AB}$$



$$\bar{E}_0 = \frac{1}{2} \times N \times (1-c) \times Z \times V_{AA} + \frac{1}{2} \times N \times c \times Z \times V_{BB}$$

$$E_m = \bar{E}_{conf} - \bar{E}_0 = \left[\frac{1}{2} \times N \times (1-c) \times Z - N_{AA} \right] \times W$$

$$W = 2 \times V_{AB} - V_{AA} - V_{BB}$$

CONCLUSION: the configurational energy of mixing depends exclusively on N_{AA} – as a configurational variable and on W – as an energetic variable

GENERALIZATION:

Within pair-interaction approximation:

n-component systems,
structures with m sublattices

$$E_m = E_m(\{N_{ij}\}, \quad i, j = 1, 2, 3, \dots, n)$$

$\frac{n^2 + n}{2} N_{ij}$ variables, $n \times m - m - n + 1 N_i^{(\mu)}$ variables

pair-interactions in
r co-ordination zones

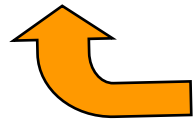
$$E_m = E_m(\{N_{ij}(r_k)\}, \quad i, j = 1, 2, 3, \dots, n; k = 1, 2, \dots, r)$$

$r \times \frac{n^2 + n}{2} N_{ij}$ variables, $n \times m - m - n + 1 N_i^{(\mu)}$ variables

Beyond pair-interaction approximation:

many-body interactions

$$E_m = E_m(\{N_{ijkl\dots}\})$$



numbers of clusters
with particular
atomic configurations

CONFIGURATIONAL FREE ENERGY OF MIXING

$$F = -k_B \times T \times \ln Z$$

$$Z = \sum_{conf} \exp\left[-\frac{\bar{E}_{conf}}{k_B T}\right] = \sum_{conf} \exp\left[-\frac{\bar{E}_0 + E_m}{k_B T}\right] = \overset{\text{constant factor}}{\downarrow} C(T) \times \sum_{conf} \exp\left[-\frac{E_m}{k_B T}\right]$$

Within the nn pair-interaction approximation:

$$Z = C(T) \times \sum_{conf} \exp\left[-\frac{E_m(N_{AA})}{k_B T}\right] = C(T) \times \sum_{N_{AA}} \left\{ \underset{\uparrow}{g(N_{AA})} \times \exp\left[-\frac{E_m(N_{AA})}{k_B T}\right] \right\}$$

number of ALL configurations showing similar values of N_{AA}

Basic thermodynamical approximation:

$$Z \approx C(T) \times \left\{ g(N_{AA}) \times \exp\left[-\frac{E_m(N_{AA})}{k_B T}\right] \right\}_{\max}$$

The partition function is approximated by its maximum term

Hence:

$$F = \left\{ E_m(N_{AA}) - k_B \times T \times \ln[g(N_{AA})] \right\}_{MIN}$$

$$F = \left\{ E_m(N_{AA}) - T \times S_{conf} \right\}_{MIN}$$

Where the functional of the configurational entropy of mixing:

$$S_{conf} = k_B \times \ln[g(N_{AA})]$$

Conclusion: the equilibrium value of the parameter N_{AA} at temperature T minimises the free energy functional F

BASIC DIFFICULTY AND THE PRINCIPAL PROBLEM OF CONFIGURATIONAL THERMODYNAMICS:

It is impossible to exactly evaluate the number $g(N_{AA})$. (*The exact solution (by Onsager) exists only for a 2-dimensional lattice*)

The same problem appears when working with many-body potentials – no exact evaluation of $g(\{N_{ijk...}\})$.

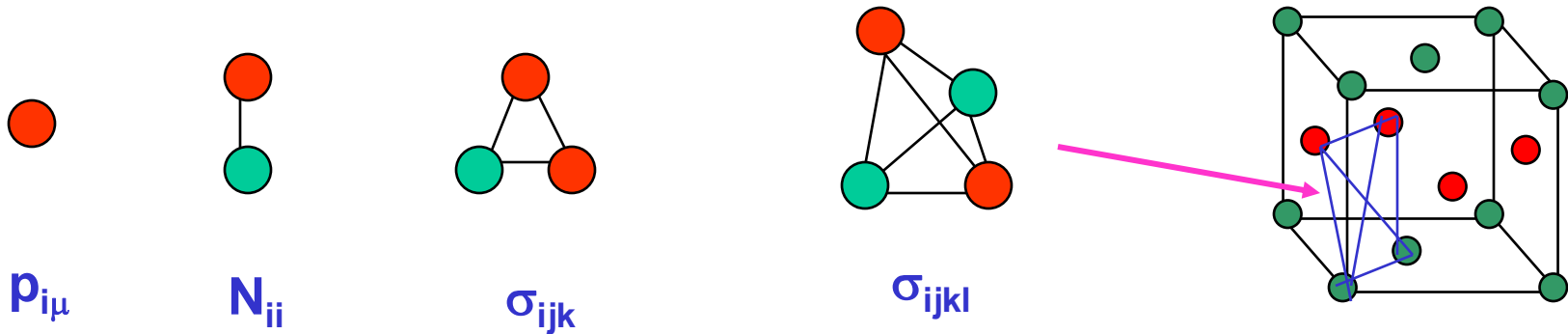
Formulation of appropriate approximation methods for the evaluation of g is one of the main tasks of the configurational thermodynamics.

CONCEPT OF CLUSTER VARIATION (CVM)

R. Kikuchi, Phys.Rev. 81, 988, (1951).

Complete description of an atomic configuration of a crystal: information on the occupation of **EACH** lattice site – unfeasible ! – but necessary for accurate determination of the free energy

General assumption of the CVM: The atomic configuration of a crystal is given in terms of **cluster variables** $\{\sigma_{ijk\dots}\}$: the probabilities that finite clusters of the lattice sites appear in particular configurations (feasible to be given explicitly).



In an effective analysis clusters up to an arbitrarily chosen biggest one are considered. The bigger is the largest cluster, the more accurate is the description. Asymptotically, the exact description is achieved if the entire crystal is taken as the biggest cluster.

The effective procedure consists of the minimisation the F functional with respect to $\{\sigma_{ijk\dots}\}$:

$$F = \left\{ E_m \left[N_{AA} \left(\{ \sigma_{ijk\dots} \} \right) \right] - k_B \times T \times \ln \left[g \left(N_{AA} \left(\{ \sigma_{ijk\dots} \} \right) \right) \right] \right\}_{MIN} \quad \leftarrow \text{in nn pair approximation}$$

Methods are developed for finding $g(\{\sigma_{ijk\dots}\})$

First, one writes down the number W of possible arrangements of all α clusters having any configurations in the system composed of N lattice sites. If there are $m_\alpha N$ such clusters in the system one has:

$$W = \frac{(m_\alpha N)!}{\prod_{\sigma_\alpha} [N_\alpha(\sigma_\alpha)]} = \frac{(N)^{m_\alpha}}{\prod_{\sigma_\alpha} \{\rho_\alpha(\sigma_\alpha) N\}^{m_\alpha}} = (\{\alpha\}_N)^{m_\alpha} \quad (16)$$

The value of W given by (16) is, however, overestimated because the α clusters overlap and, therefore, the subclusters of α contained in the overlapping volumes count too many times. The desired correction is obtained in recursion:

First an $\alpha-1$ cluster is considered. Let $n_\alpha^{\alpha-1}$ denote the number of times the $\alpha-1$ cluster is contained in an α -one. If W is given by (16) the $\alpha-1$ cluster is counted $(\{\alpha-1\}_N)^{m_\alpha n_\alpha^{\alpha-1}}$ times instead of $(\{\alpha-1\}_N)^{m_{\alpha-1}}$. The corrected value of W is thus given by:

$$W = (\{\alpha\}_N)^{m_\alpha} \times \frac{(\{\alpha-1\}_N)^{m_{\alpha-1}}}{(\{\alpha-1\}_N)^{m_\alpha n_\alpha^{\alpha-1}}} = (\{\alpha\}_N)^{m_\alpha a_\alpha} \times (\{\alpha-1\}_N)^{m_{\alpha-1} a_{\alpha-1}} \quad (17)$$

where:

$$a_\alpha = 1 \text{ for the basic cluster}$$

$$\text{and } m_{\alpha-1} \times a_{\alpha-1} = m_{\alpha-1} - m_\alpha \times n_\alpha^{\alpha-1} \quad (18)$$

In the next step similar procedure is applied to the subcluster $\alpha-2$, then to $\alpha-3$, etc. As a result, after having applied the Stirling formula, the configurational entropy is given by:

$$S_p = N \times k \times \sum_{\nu=1}^{\alpha} m_\nu a_\nu \sum_{\sigma_\nu} \rho_\nu(\sigma_\nu) \ln \rho_\nu(\sigma_\nu) \quad (19)$$

with the coefficients a_ν determined by the system of recursive equations (18).

“0th” (Bragg-Williams) approximation:

B.J. Bragg, E.J. Williams, Proc.Roy.Soc., A151, 540, (1935); A152, 231, (1935)

The biggest cluster: a single lattice site



Cluster variables: $p_{A1}, p_{A2}, p_{B1}, p_{B2} \Rightarrow \eta$

Basic approximation:

$$\langle N_{AA} \rangle = N_A^{(1)} \times Z \times \frac{N_A^{(2)}}{\frac{1}{2} \times N} = \frac{1}{2} \times N \times Z \times [(1-c)^2 - c^2 \times \eta^2]$$

The approximation consists of the negligence of pair-correlations and relates N_{AA} to η - which, as was shown, is not true !

The approximation yields:

$$E_m = \bar{E}_{conf} - \bar{E}_0 = \left[\frac{1}{2} \times N \times (1-c) \times Z - N_{AA} \right] \times W$$

$$E_m = \frac{1}{2} \times N \times Z \times c \times [1 + c(\eta^2 - 1)] \times W$$

The approximation yields:

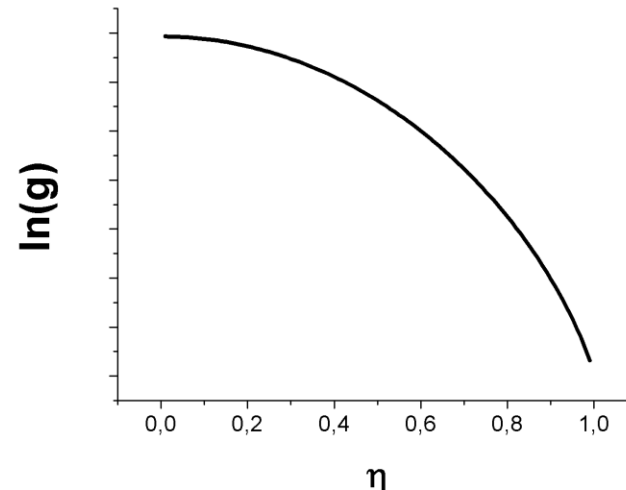
$$E_m = \frac{1}{2} \times N \times Z \times c \times [1 + c(\eta^2 - 1)] \times W = E_m(\eta)$$

and:

$$g(\eta) = g(\{N_i^{(\mu)}\}) = \frac{N^{(1)}! N^{(2)}!}{N_A^{(1)}! N_A^{(2)}! N_B^{(1)}! N_B^{(2)}!}$$

Stirling formula yields:

$$\begin{aligned} \ln[g(\eta)] \approx & \\ & -\frac{1}{2} N \times [(c\eta + 1 - c) \times \ln(c\eta + 1 - c) \\ & + (-c\eta + c) \times \ln(-c\eta + c) \\ & + (-c\eta + 1 - c) \times \ln(-c\eta + 1 - c) \\ & + (c\eta + c) \times \ln(c\eta + c)] + const \end{aligned}$$



$g(\eta)$ is a **DECREASING** function of η

$$F = \{E_m(\eta) - k_B \times T \times \ln[g(\eta)]\}_{MIN}$$

$$E_m(\eta) = \frac{1}{2} \times N \times Z \times c \times [1 + c \times (\eta^2 - 1)] \times W$$

$W > 0$: increasing function of η

$W < 0$: decreasing function of η

decreasing function of η

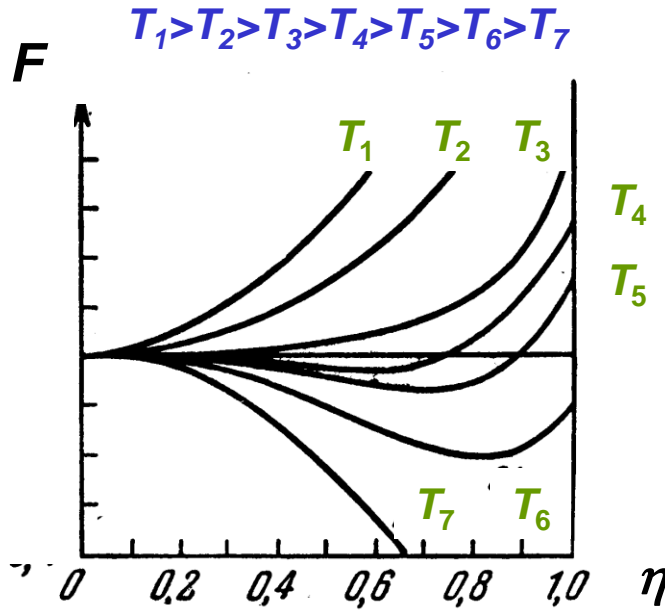
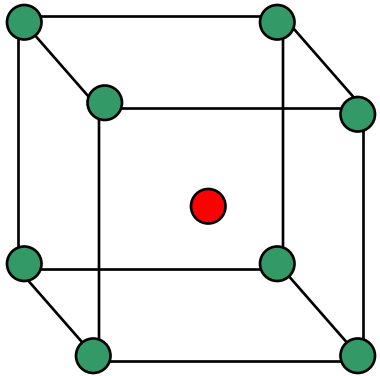
CONCLUSION:

If $W > 0$, $F = F(\eta=0)$ – no atomic ordering at any temperature

If $W < 0$, $F = F(\eta=1)$ at $T=0$ K – atomic ordering within a finite range of temperatures.

What happens when $W < 0$?

B2 superstructure:



At $T \geq T_3$ $F_{min} = F_{min}(\eta=0)$

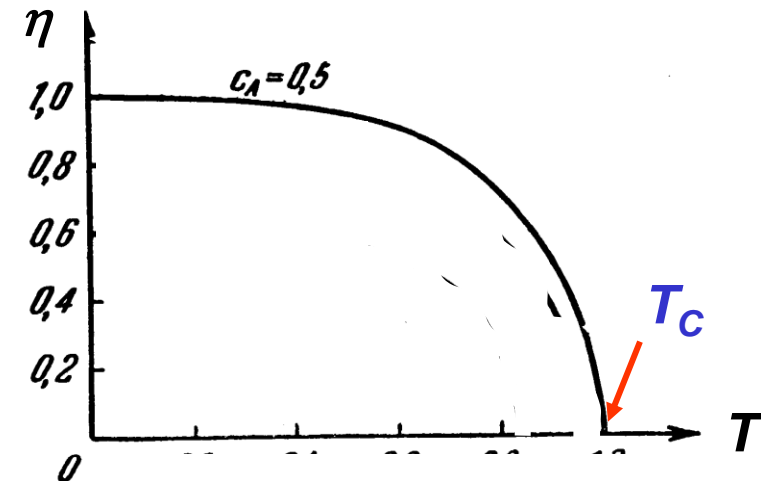
At $T \leq T_4$ $F_{min} = F_{min}(\eta > 0)$

Only one single minimum of F appears !

Consequently:

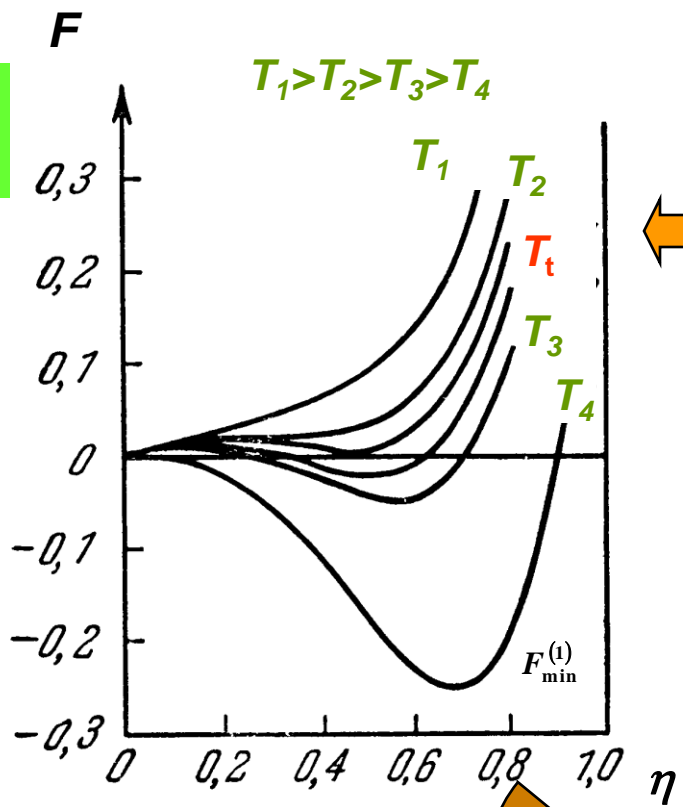
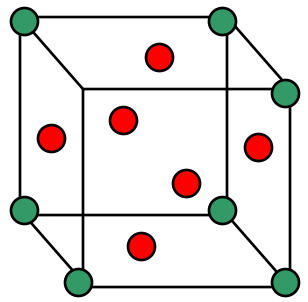
T_C evaluated from the equations:

$$\begin{cases} \frac{\partial F}{\partial \eta}(T_C, \eta = 0) = 0 \\ \frac{\partial^2 F}{\partial \eta^2}(T_C, \eta = 0) = 0 \end{cases} \rightarrow T_C = -\frac{16c(1-c)}{k_B} \times W$$



Continuous "order-disorder" phase transition at $T = T_C$

L1₂ superstructure:



two minima of $F(\eta)$

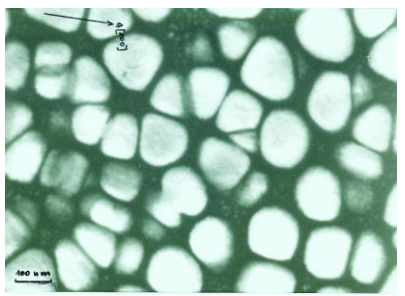
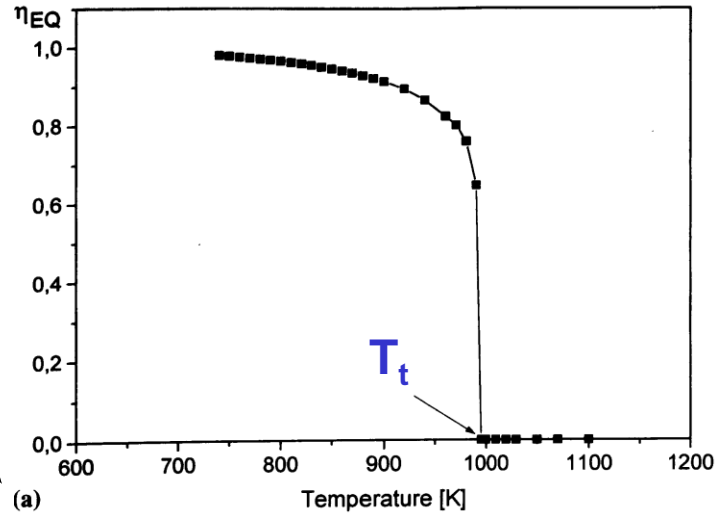
$T \geq T_2: F_{\min} = F_{\min}(\eta=0)$

$T < T_2: F_{\min}^{(1)}(\eta=0), F_{\min}^{(2)}(\eta>0);$
 $F_{\min}^{(2)}(\eta>0) > F_{\min}^{(1)}(\eta=0)$

$T = T_t: F_{\min}^{(2)}(\eta>0) = F_{\min}^{(1)}(\eta=0)$

$T < T_t: F_{\min}^{(2)}(\eta>0) < F_{\min}^{(1)}(\eta=0)$

$T \leq T_c: F_{\min} = F_{\min}(\eta>0)$

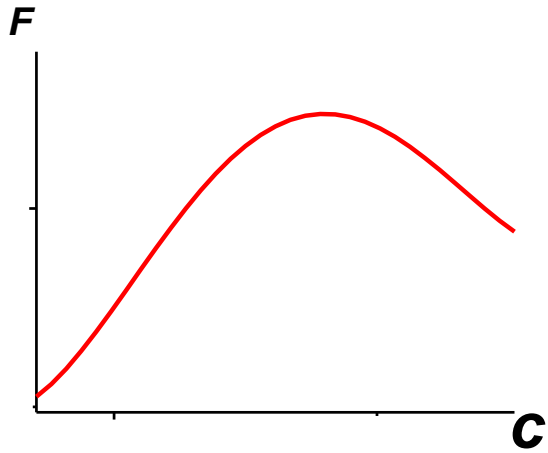


Ordered ($\eta > 0$) and disordered ($\eta = 0$) phases coexist as long as F shows two minima

Discontinuous "order-disorder" phase transition at $T = T_t$

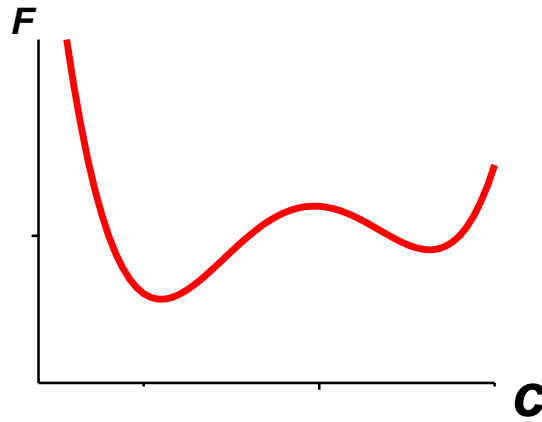
What happens when $W > 0$?

$$\eta = 0$$



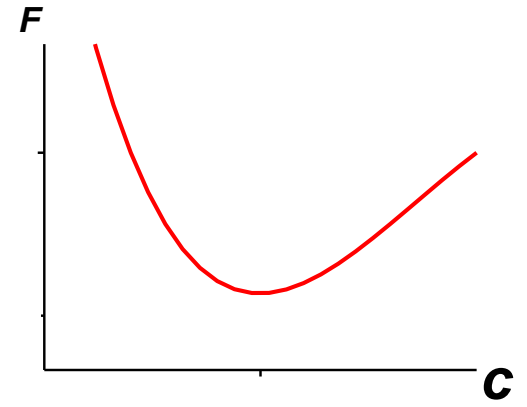
T_1

<



T_2

<



T_3

Interpretation: two-phase equilibrium: lever rule

Entire system: A-B:

$$N = N^{(1)} + N^{(2)}$$

$$N_A = N_A^{(1)} + N_A^{(2)}$$

$$N_B = N_B^{(1)} + N_B^{(2)}$$

$$N_B = C_0 N$$

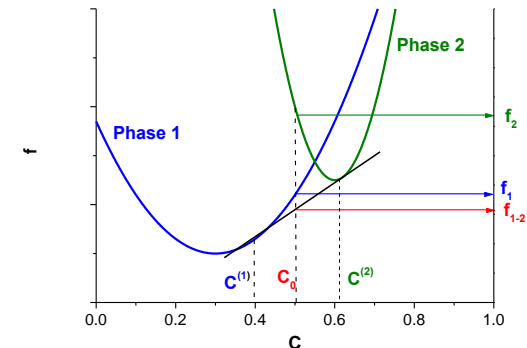
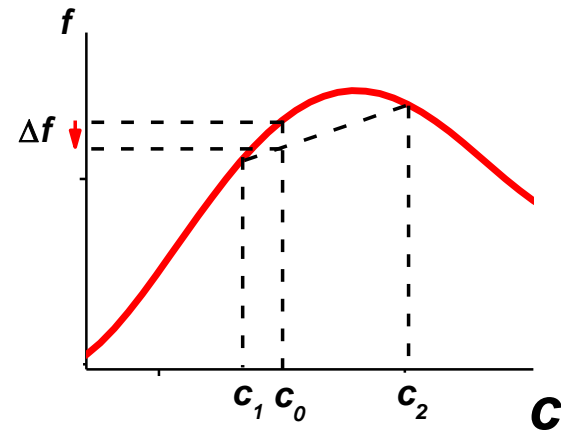
Phase 1:	Phase 2:
$N_A^{(1)}, N_B^{(1)}$	$N_A^{(2)}, N_B^{(2)}$
$N^{(1)} = N_A^{(1)} + N_B^{(1)}$	$N^{(2)} = N_A^{(2)} + N_B^{(2)}$
$N_B^{(1)} = c^{(1)} N^{(1)}$	$N_B^{(2)} = c^{(2)} N^{(2)}$
f_1 – free energy per one molecule	f_2 – free energy per one molecule

Hence:

$$N^{(1)} = \frac{c^{(2)} - c_0}{c^{(1)} - c^{(2)}} \times N, \quad N^{(2)} = \frac{c_0 - c^{(1)}}{c^{(1)} - c^{(2)}} \times N$$

$$f_{1-2}(c_0) = \frac{1}{N} [N^{(1)} f_1(c^{(1)}) + N^{(2)} f_2(c^{(2)})] =$$

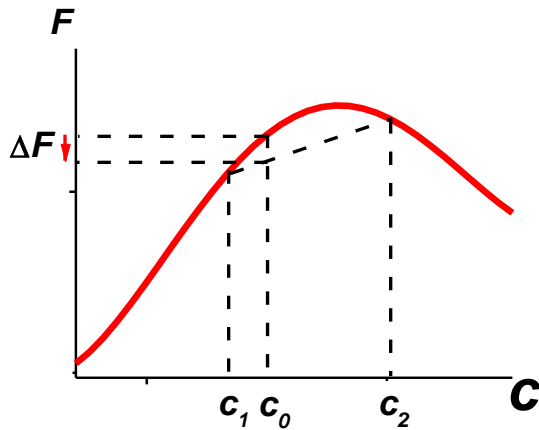
$$= \frac{c^{(2)} - c_0}{c^{(1)} - c^{(2)}} \times f_1(c^{(1)}) + \frac{c_0 - c^{(1)}}{c^{(1)} - c^{(2)}} \times f_2(c^{(2)})$$



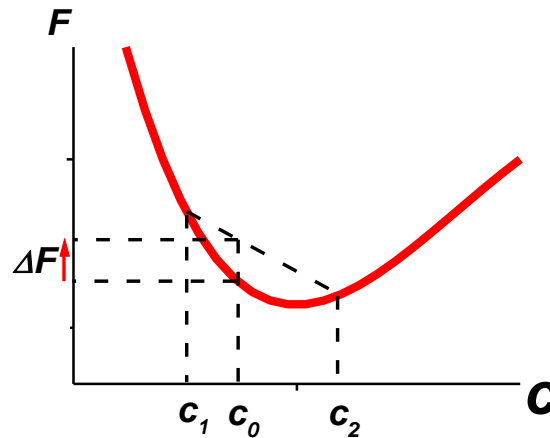
DECOMPOSITION OF A BINARY SOLUTION A-B INTO TWO PHASES:

c_0 – concentration of B-atoms in the homogeneous solution (before the decomposition)

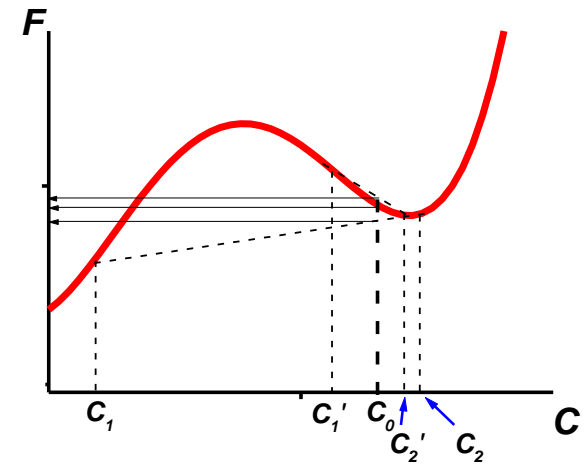
c_1, c_2 – concentrations of B-atoms in the two phases, into which the solution decomposes



Decomposition **DECREASES** the free energy of the system



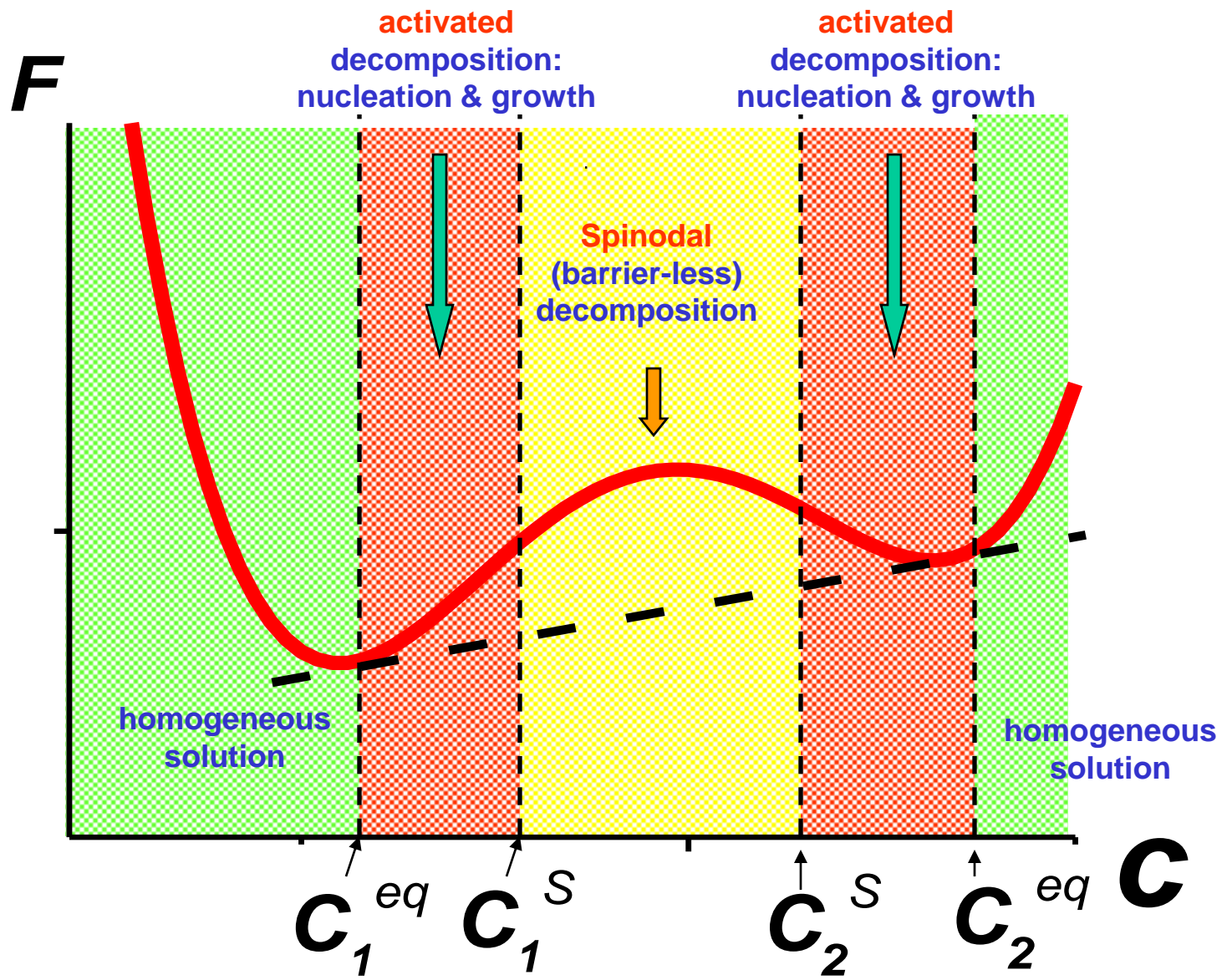
Decomposition **INCREASES** the free energy of the system



Decomposition into c_1' and c_2' **INCREASES** F , but the continuation to c_1 and c_2 finally **DECREASES** the free energy of the system

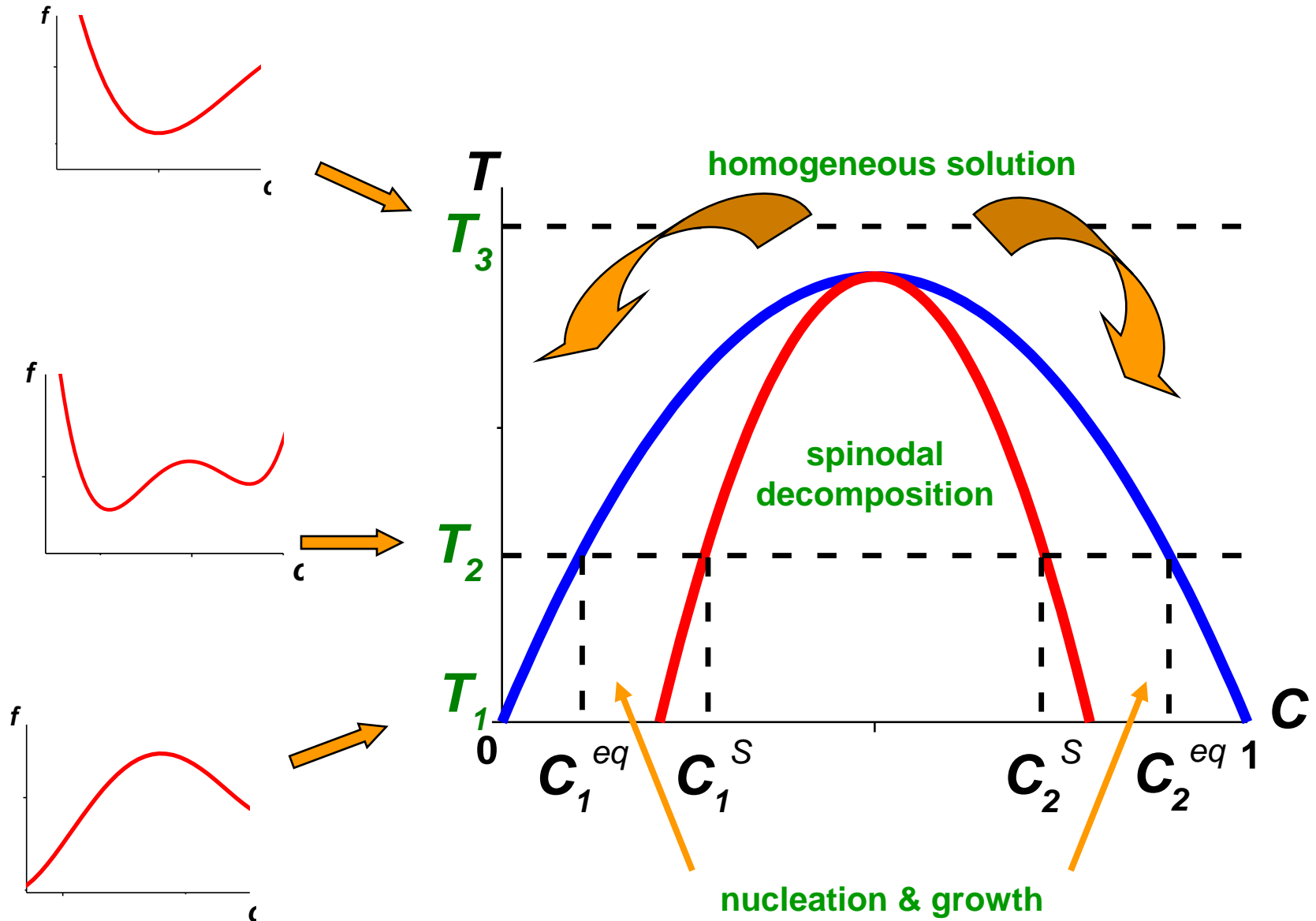
SPONTANEOUS AND ACTIVATED DECOMPOSITION

$T = T_2$



The solution with $C_1^{eq} < C_0 < C_2^{eq}$ decomposes into two phases with concentrations equal to C_1^{eq} and C_2^{eq}

MISCIBILITY GAP AND SPINODAL



THEORY OF SPINODAL DECOMPOSITION

Free energy of an inhomogeneous system
CONTINUOUS MEDIUM approach:

$$F(c) = \frac{N}{V} \times \int f(c) \times d^3r \quad c - \text{average concentration}$$

$$f(c) = f\left(c, \left\{\frac{\partial c}{\partial \vec{r}}\right\}, \left\{\frac{\partial c}{\partial x_i} \frac{\partial c}{\partial x_j}\right\}, \left\{\frac{\partial^2 c}{\partial x_i \partial x_j}\right\}, \dots\right) \quad \leftarrow \text{free energy per one atom}$$

$$f(c) \approx f_0(c) + L_i \frac{\partial c}{\partial x_i} + \kappa_{ij}^{(1)} \frac{\partial^2 c}{\partial x_i \partial x_j} + \kappa_{ij}^{(2)} \frac{\partial c}{\partial x_i} \frac{\partial c}{\partial x_j} + \dots$$



free energy per one atom
for a homogeneous system

Cubic crystal:

inversion: $\mathbf{x}_j \rightarrow -\mathbf{x}_j$: $\Rightarrow L_i \equiv 0$

$\frac{\pi}{2}$ rotation: $\mathbf{x}_i \rightarrow \mathbf{x}_j$: $\Rightarrow \begin{cases} \kappa_{ij}^{(1)} = \kappa^{(1)} \delta_{ij} = \frac{\partial f}{\partial (\nabla^2 c)} \delta_{ij} \\ \kappa_{ij}^{(2)} = \kappa^{(2)} \delta_{ij} = \frac{\partial^2 f}{\partial (\nabla c)^2} \delta_{ij} \end{cases}$



$$F(c) = \frac{N}{V} \int_V dV \left[f_0(c) + \kappa^{(1)} \nabla^2 c + \kappa^{(2)} (\nabla c)^2 + \dots \right]$$

$$\kappa^{(1)} \nabla^2 c = \nabla \cdot (\kappa^{(1)} \nabla c) - \frac{\partial \kappa^{(1)}}{\partial c} (\nabla c)^2$$

but:

$$\int_V dV \left[\kappa^{(1)} \nabla^2 c + \frac{\partial \kappa^{(1)}}{\partial c} (\nabla c)^2 \right] = \oint_S [\kappa^{(1)} \nabla c \cdot \vec{n}] dS = 0$$

hence

$$\kappa^{(1)} \nabla^2 c = - \frac{\partial \kappa^{(1)}}{\partial c} (\nabla c)^2$$

and:

$$F(c) = \frac{N}{V} \int_V dV [f_0(c) + \kappa (\nabla c)^2 + \dots], \quad \kappa = - \frac{\partial \kappa^{(1)}}{\partial c} + \kappa^{(2)}$$

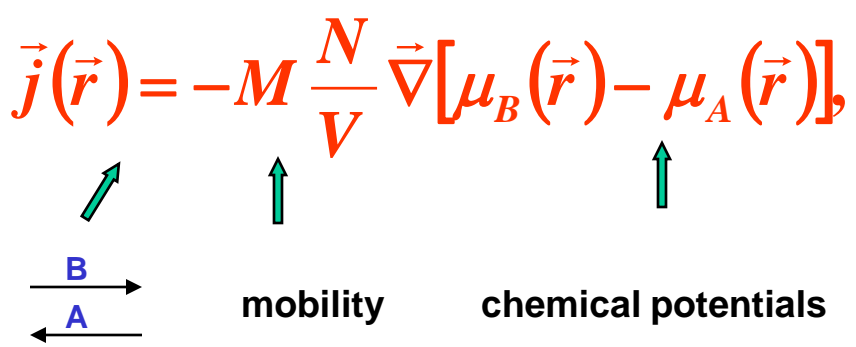
For systems which are homogeneous at any temperature there must hold:

$$\kappa > 0$$

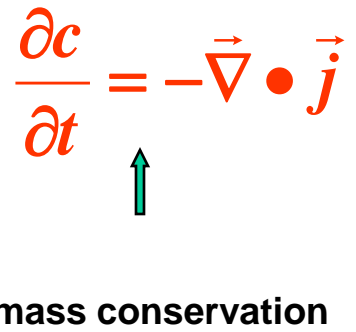
Diffusion in inhomogeneous system:

General equation for diffusion flux density:

$$\vec{j}(\vec{r}) = -M \frac{N}{V} \vec{\nabla} [\mu_B(\vec{r}) - \mu_A(\vec{r})],$$

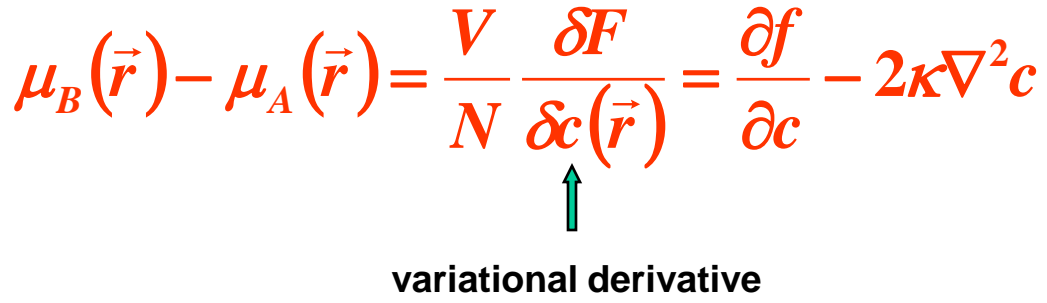


$$\frac{\partial c}{\partial t} = -\vec{\nabla} \cdot \vec{j}$$



$$\mu_B(\vec{r}) - \mu_A(\vec{r}) = \frac{\Delta F}{\Delta n_B(\vec{r})}, \left(\Delta n_B(\vec{r}) \rightarrow 0 \Big|_{\Delta c \rightarrow 0 \wedge \Delta^3 r \rightarrow 0} \right)$$

$$\mu_B(\vec{r}) - \mu_A(\vec{r}) = \frac{V}{N} \frac{\delta F}{\delta c(\vec{r})} = \frac{\partial f}{\partial c} - 2\kappa \nabla^2 c$$



hence

$$\frac{\partial c}{\partial t} = M \nabla^2 \left[\frac{\partial f}{\partial c} - \kappa \nabla^2 c \right]$$

linearisation:

$$c(\vec{r}) = c_0 + u(\vec{r}), \quad u(\vec{r}) \ll c_0, \quad \frac{\partial f}{\partial c} = \left. \frac{\partial f}{\partial c} \right|_{c_0} + \left. \frac{\partial^2 f}{\partial c^2} \right|_{c_0} \times u + \dots$$

 average concentration

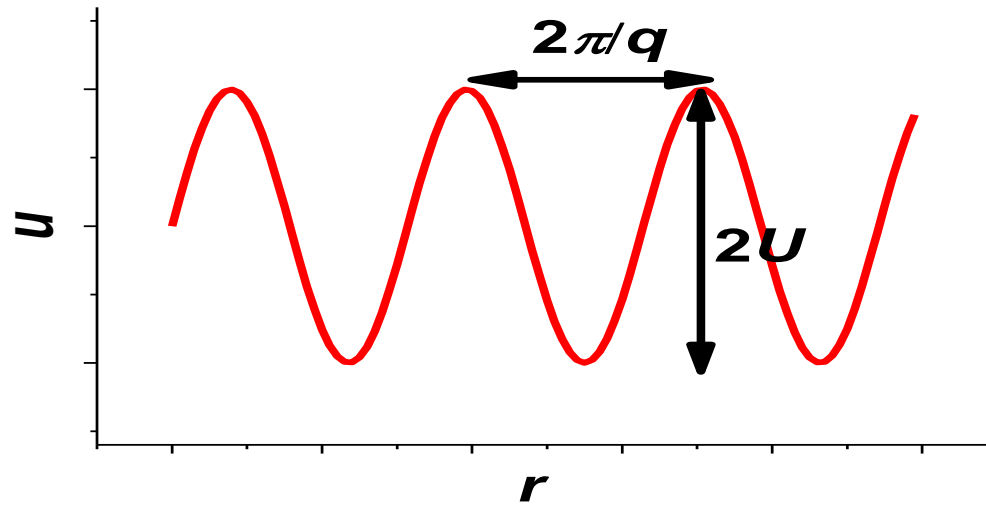
$$\frac{\partial u}{\partial t} = M \nabla^2 \left[\left. \frac{\partial^2 f}{\partial c^2} \right|_{c_0} - \kappa \nabla^2 \right] u$$

 linear differential equation

Assumption:

$$u(\vec{r}, t) = \int U(\vec{q}, t) \times e^{i\vec{q}\vec{r}} d\vec{q} \quad \leftarrow \text{Fourier transform}$$

\uparrow
 q wave amplitude



The resulting equation for U:

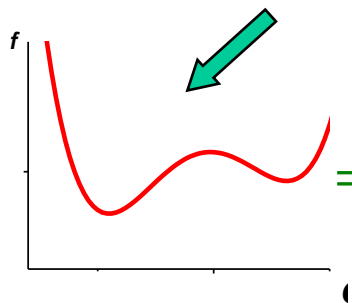
$$\frac{\partial U(\vec{q}, t)}{\partial t} = -Mq^2 \left[\frac{\partial f}{\partial c^2} \Big|_{c_0} + \kappa q^2 \right] U$$

solution:

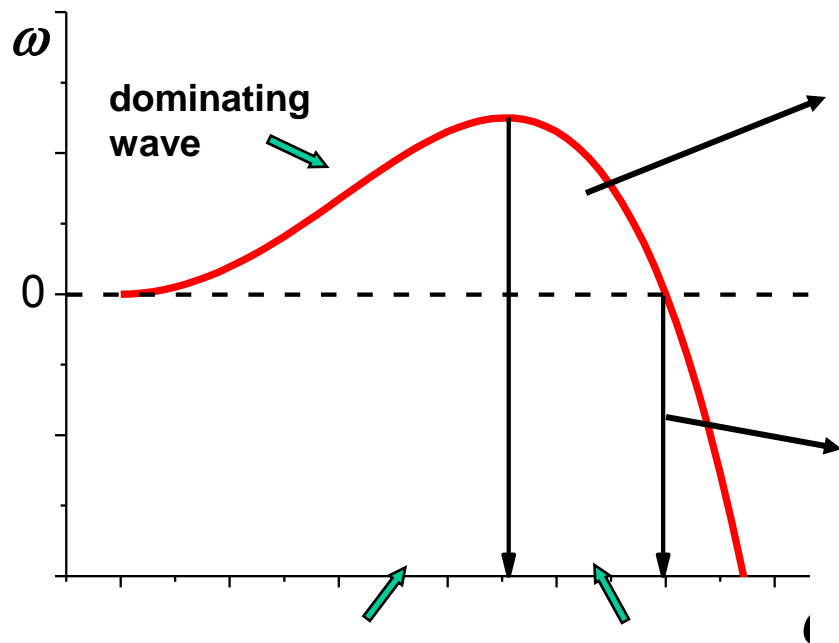
$$U(\vec{q}, t) = U(\vec{q}, t = 0) \times e^{\omega(\vec{q})t}$$

$$\omega(\vec{q}) = M\kappa q^2 \left(-\frac{1}{2\kappa} \frac{\partial^2 f}{\partial c^2} \Big|_{c_0} - q^2 \right)$$

Solution for $\frac{\partial^2 f}{\partial c^2} < 0$

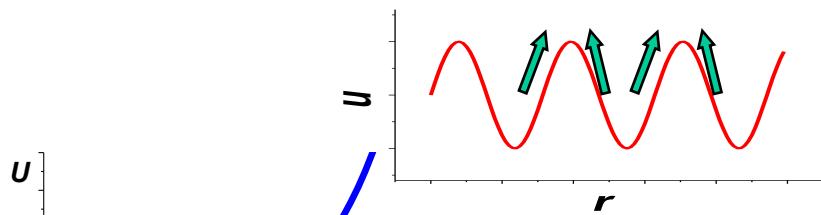


⇒ inside the spinodal curve !



$$\pm \sqrt{-\frac{1}{4\kappa} \frac{\partial^2 f}{\partial c^2} \Big|_{c_0}}$$

$$q_c = \pm \sqrt{-\frac{1}{2\kappa} \frac{\partial^2 f}{\partial c^2} \Big|_{c_0}}$$



up-hill diffusion

