

# 1 Introduction

We have seen that energetic and entropic forces can generate interactions of the order of  $k_B T$  or more. Under these conditions particles can condense into a dense state which can be a liquid or a crystal phase. Later on we will see that other (so-called) mesophases can exist in colloidal and macromolecular systems. For the time being let's review the conditions for the onset of a liquid phase and the location in the phase diagram of the gas-liquid coexistence. For didactic reasons, we first study the thermodynamic stability of a symmetric mixture on lattice and then we will move to the gas-liquid problem. We will tackle this topic in the so-called mean-field approximation. More elaborate treatments of phase separation phenomena are provided in the class of critical phenomena. The mean-field approximation, while crude, provides a good intuition of the phenomenon.

## 2 Mean field solution of the lattice model for binary mixtures

Consider a binary mixture of species  $A$  and  $B$  on a lattice. The system is assumed to be incompressible, meaning that the sum of the number of  $A$  sites  $N_A$  and the number of  $B$  sites  $N_B$  is equal to the number of lattice sites  $N$ .

Defining an occupation number on the lattice  $n_i$  as 0 if the site is occupied by an  $A$  atom and as 1 if it is occupied by a  $B$  atom, the Hamiltonian of the model can be written as

$$H = - \sum_{ij} [\epsilon_{AA}(1 - n_i)(1 - n_j) + \epsilon_{AB}(1 - n_i)n_j + \epsilon_{AB}n_i(1 - n_j) + \epsilon_{BB}n_in_j]$$

with some algebra,

$$\begin{aligned} & [\epsilon_{AA}(1 - n_i)(1 - n_j) + \epsilon_{AB}(1 - n_i)n_j + \epsilon_{AB}n_i(1 - n_j) + \epsilon_{BB}n_in_j] = \\ & [\epsilon_{AA}(1 - n_j) - \epsilon_{AA}n_i(1 - n_j) + \epsilon_{AB}n_j - \epsilon_{AB}n_in_j - \epsilon_{AB}n_i + \epsilon_{AB}n_i + \epsilon_{AB}n_i(1 - n_j) + \epsilon_{BB}n_in_j - \epsilon_{BB}n_i + \epsilon_{BB}n_i] = \\ & [n_i(1 - n_j)(-\epsilon_{AA} + \epsilon_{AB} + \epsilon_{AB} - \epsilon_{BB}) + \epsilon_{AA}(1 - n_j) + \epsilon_{AB}n_j - \epsilon_{AB}n_i + \epsilon_{BB}n_i] = \\ & [n_i(1 - n_j)(-\epsilon_{AA} - \epsilon_{BB} + 2\epsilon_{AB}) - \epsilon_{AA}n_j + \epsilon_{BB}n_i + \epsilon_{AA}] \end{aligned}$$

Considering that in the sum  $\sum_{ij}$  there are  $N\gamma/2$  elements and that  $\sum_{ij} n_i = N\gamma \sum_i n_i$

$$H = (\epsilon_{AA} + \epsilon_{BB} - 2\epsilon_{AB}) \sum_{ij} n_i(1 - n_j) - 2\gamma \frac{\epsilon_{AA} - \epsilon_{BB}}{4} \sum_i n_i - N\gamma \frac{\epsilon_{AA}}{2}$$

which for simplicity we rewrite as (assuming that  $\epsilon_{AA} = \epsilon_{BB}$ , and neglecting the constant value  $N\gamma \frac{\epsilon_{AB}}{2}$ )

$$H = \epsilon \sum_{ij} n_i(1 - n_j)$$

Note that if  $\epsilon \equiv \epsilon_{AA} + \epsilon_{BB} - 2\epsilon_{AB} < 0$  mixing will be favoured. Opposite behavior (demixing) is expected when  $\epsilon > 0$ .

In a very basic mean field approach, the correlation between different sites is treated equally for all sites (fluctuations are neglected). In this case, each generic site  $i$  has an identical probability of being occupied by  $A$  or  $B$ , independently from nearby sites. Hence, for each  $B$  site, the probability that one of the  $\gamma$  adjacent sites is occupied by  $A$  is  $N_A/N$ . Then we can estimate the number of  $BA$  pairs in the lattice as  $N_B\gamma N_A/N$ . Hence, we can approximate

$$\sum_{ij} n_i(1 - n_j) \approx N_B\gamma \frac{N_A}{N}$$

and write an approximate partition function as

$$Z(T, N_B) = \frac{N!}{(N - N_B)!N_B!} e^{-\beta\epsilon N_B\gamma \frac{N - N_B}{N}}$$

The corresponding free energy per lattice site  $\beta f$  is

$$\beta f = \frac{\beta F}{N} = -\frac{\ln Z(T, N_B)}{N} = \beta\epsilon \frac{N_B}{N} \gamma \frac{N - N_B}{N} - \frac{1}{N} (\ln N! - \ln(N - N_B)! - \ln N_B!)$$

Using Stirling, and defining  $\phi \equiv \frac{N_B}{N}$ , (and using  $N \ln N = [N_B + (N - N_B)] \ln N$ )

$$\beta f = \beta\epsilon\gamma\phi(1 - \phi) + \phi \ln \phi + (1 - \phi) \ln(1 - \phi)$$

where we can easily recognize the energetic and the entropic contributions. Since  $\lim_{x \rightarrow 0} x \ln x = 0$ , entropy contributes to the free-energy with a symmetric negative terms, the dominant one for  $\beta \rightarrow 0$ . On cooling, the energy contribution increases its importance and it changes the concavity of the free energy at a critical  $\beta$  values.

Thanks to the symmetry  $\phi$  vs  $1 - \phi$  (as clearly shown also in the figure), we immediately see that the critical  $\phi$  is  $\phi_c = 0.5$ . We can then attempt to expand the free energy around  $\phi_c$  to estimate  $T_c$  and look at the way the critical behavior arises. To do so we define  $M \equiv \phi - \phi_c$ , and expand  $f$  around  $M = 0$ .

Let's first look at the Taylor expansion of the entropy. The first four derivatives are

$$\frac{1}{1!}\phi' = \ln \phi - 1 - \ln(1 - \phi) + 1 \quad \phi'(\phi = 0.5) = 0 \quad (1)$$

$$\frac{1}{2!}\phi'' = \frac{1}{2} \left( \frac{1}{\phi} + \frac{1}{1 - \phi} \right) \quad \phi''(\phi = 0.5) = 4 \quad (2)$$

$$\frac{1}{3!}\phi''' = \frac{1}{6} \left( -\frac{1}{\phi^2} + \frac{1}{(1 - \phi)^2} \right) \quad \phi'''(\phi = 0.5) = 0 \quad (3)$$

$$\frac{1}{4!}\phi'''' = \frac{1}{24} \left( \frac{2}{\phi^3} - \frac{2}{(1 - \phi)^3} \right) \quad \phi''''(\phi = 0.5) = 32 \quad (4)$$

such that

$$\phi \ln \phi + (1 - \phi) \ln(1 - \phi) \approx -\ln 2 + 2M^2 + \frac{4}{3}M^4$$

Since  $\phi(1 - \phi)$  expanded around  $\phi = 0.5$  gives  $\phi(1 - \phi) \approx \frac{1}{4} + (1 - 2\phi)M + \frac{1}{2}(-2)M^2 = \frac{1}{4} - M^2$

$$\beta f(M) \approx \beta f(0) - \beta\epsilon\gamma M^2 + 2M^2 + \frac{4}{3}M^4$$

and finally

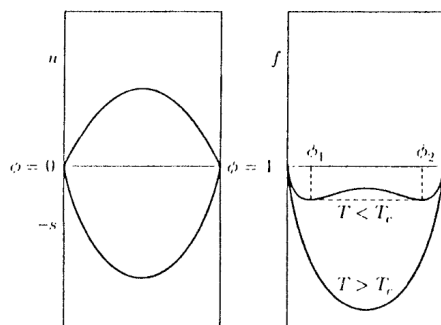
$$\beta f(M) \approx \beta f(0) + (-\beta\epsilon\gamma + 2)M^2 + \frac{4}{3}M^4$$

This shows that when the concavity of  $\beta f$  changes when

$$-\beta\epsilon\gamma + 2 = 0 \quad \rightarrow \quad k_B T = \frac{\epsilon\gamma}{2}$$

and we can rewrite

$$f(M) \approx f(0) + 2k_B(T - T_c)M^2 + \frac{4k_B T}{3}M^4$$



**Figure 4.1.** Free energy of a symmetric mixture. The left panel shows the entropic (convex) and energetic (concave) contributions,  $-s$  and  $u$ , to the free energy. The resulting free energy per particle,  $f = u - Ts$  is shown on the right for  $T > T_c$  and  $T < T_c$ . For  $T < T_c$ , systems with  $\phi_1 < \phi < \phi_2$  are not thermodynamically stable.

### 3 Lattice gas

In a similar way we can tackle the problem of a system of interacting particles, where interaction is limited to nearest neighbour positions. In a lattice of connectivity  $\gamma$ , the lattice-gas Hamiltonian is

$$H = -\epsilon \sum_{i,j} n_i n_j$$

where  $\epsilon > 0$  is the interaction energy and  $n_i = 0, 1$  indicate the presence or absence of a particle in site  $i$ . The sum goes over all nearest neighbour sites in the lattice  $N\gamma/2$ .

Exactly as before we can write the mean-field free energy as (indicating with  $N_P$  the number of occupied sites in the lattice), based on the mean-field partition function

$$Z = \frac{N!}{(N - N_P)!N_P!} e^{\beta\epsilon N_P \frac{N_P}{N} \frac{\gamma}{2}}$$

$$\beta f = \frac{\beta F}{N} = -\frac{\ln Z(T, N_B)}{N} = -\beta\epsilon \frac{N_P}{N} \gamma \frac{N_P}{2N} - \frac{1}{N} (\ln N! - \ln(N - N_P)! - \ln N_P!)$$

and as before we find

$$\beta f = -\frac{\beta\epsilon\gamma}{2}\phi^2 + \phi \ln \phi + (1 - \phi) \ln(1 - \phi)$$

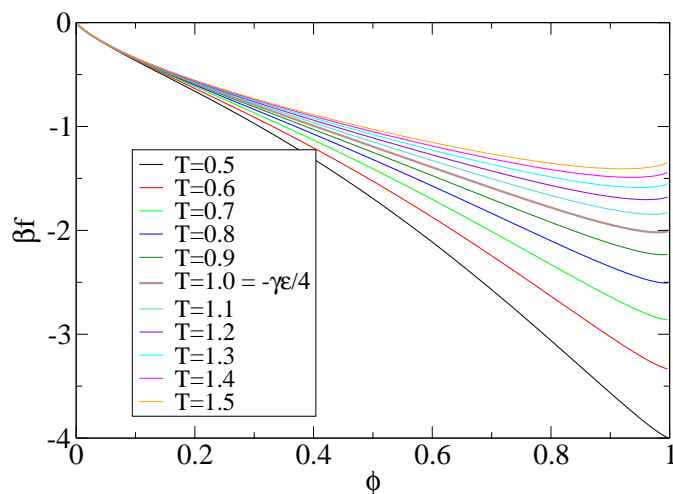


Fig. 3 shows  $\beta f$  for different  $T$  when  $\gamma = 4$ . As before, we observe that there is a temperature below which the concavity of  $\beta f$  changes from positive to negative. To find this temperature quickly let us use the same expansion around  $\phi = 0.5$  that we indicate with the symbol  $\phi_c$ .

As we have seen before, the first derivatives of  $g = \phi \ln \phi + (1 - \phi) \ln(1 - \phi)$  are

$$\frac{1}{1!}g' = \ln \phi - \ln(1 - \phi) \quad \phi'(\phi = 0.5) = 0 \quad (5)$$

$$\frac{1}{2!}g'' = \frac{1}{2} \left( \frac{1}{\phi} + \frac{1}{1 - \phi} \right) \quad \phi''(\phi = 0.5) = 4 \quad (6)$$

$$\frac{1}{3!}g''' = \frac{1}{6} \left( -\frac{1}{\phi^2} + \frac{1}{(1 - \phi)^2} \right) \quad \phi'''(\phi = 0.5) = 0 \quad (7)$$

$$\frac{1}{4!}g'''' = \frac{1}{24} \left( \frac{2}{\phi^3} + \frac{2}{(1 - \phi)^3} \right) \quad \phi''''(\phi = 0.5) = 32 \quad (8)$$

Then

$$\beta f(\phi) \approx -\frac{\beta\epsilon\gamma}{2}(\phi - \phi_c + \phi_c)^2 - \ln 2 + 2(\phi - \phi_c)^2 + \frac{4}{3}(\phi - \phi_c)^4$$

and including all constant in  $f(\phi_c)$  and expanding the first square bracket

$$\beta f(\phi) \approx \beta f(\phi_c) - \frac{\beta\epsilon\gamma}{2}(\phi - \phi_c)2\phi_c - \frac{\beta\epsilon\gamma}{2}(\phi - \phi_c)^2 + 2(\phi - \phi_c)^2 + \frac{4}{3}(\phi - \phi_c)^4$$

The second derivative respect to  $(\phi - \phi_c)$  gives

$$\frac{d^2\beta f(\phi)}{d(\phi - \phi_c)^2} = 2 \left( 2 - \frac{\beta\epsilon\gamma}{2} \right) + 16(\phi - \phi_c)^2$$

which shows that the concavity becomes negative for the first time when  $\phi = \phi_c$  (so that the last positive term vanishes) when

$$\epsilon\beta\gamma - 4 < 0 \quad \rightarrow \quad T < T_c \quad \text{with} \quad k_B T_c = \frac{\epsilon\gamma}{4}$$

While the behavior of the free energy could at first sight looks different from the one of the mixture (there is a linear term in the free-energy beside the quadratic and the quartic term), in terms of concavity (second derivative) the two expressions are quite similar. They both show that below a critical temperature, a region of negative curvature appears. Later on, we will discuss the meaning of this region. First, let's investigate the first model proposed by a young Ph.D. student to describe the onset of a liquid phase in simple gases.

## 4 van der Waals: hard-spheres plus mean-field attraction

Il modello di van der Waals mostra come un approccio fisico consenta di capire gli elementi essenziali di un processo. Nel caso specifico van der Waals sviluppo un modello semplificato per spiegare la condensazione dei gas e la formazione dello stato liquido. Guardiamo questo modello in modo schematico.

Consideriamo un gas di sfere dure, di diametro  $\sigma$ . Se  $\sigma = 0$ , la funzione di partizione, per quel che riguarda le coordinate, darebbe un contributo  $V^N$ . In prima approssimazione possiamo assumere che in condizioni diluite,  $V^N$  diventi  $V_{\text{accessibile}}^N$ . Il volume accessibile  $V_{\text{accessibile}} = V - Nb$  dove  $b$  e' il volume escluso dalla presenza di una sfera. Poiche' la distanza minima tra due sfere e'  $\sigma$  il volume escluso e'  $4\pi/3\sigma^3$ . Se associamo questo volume alle due sfere, possiamo dire che ciascuna sfera esclude un volume  $V_b = 2\pi/3\sigma^3$  e

$$Z(V, N, T) = \frac{(V - Nb)^N}{\lambda^{3N} N!}$$

Per considerare l' attrazione tra le particelle assumiamo che ogni particella interagisca con la stessa intensita'  $-\epsilon$  con tutte le particelle all' interno di un raggio  $R_c$ . Possiamo allora scrivere che l' energia della particella, trascurando le fluttuazioni spaziali, e'

$$E_i = -\epsilon \frac{4}{3} \pi R_c^3 \frac{N}{V}$$

e l' energia  $E$  del sistema  $E = \frac{1}{2} \sum_i E_i$

$$E = \frac{1}{2} \sum_i E_i = -N\epsilon \frac{2}{3} \pi R_c^3 \frac{N}{V} \equiv -a \frac{N^2}{V}$$

con  $a$  costante positiva.

La funzione di partizione ora diviene

$$Z(V, N, T) = \frac{(V - Nb)^N}{\lambda^{3N} N!} e^{\beta a \frac{N^2}{V}} \quad \rightarrow \quad \beta F = -\ln Z(V, N, T) = -N \ln \left[ \frac{V - Nb}{\lambda^3} \right] - \beta a \frac{N^2}{V} - \ln N!$$

Per vedere se esiste un punto critico, occorre cercare se esiste un punto (nel piano T,V) in cui la concavita' della energia libera cambia. Matematicamente questo vuol dire cercare il punto in cui derivata seconda e derivata terza rispetto al volume sono nulle. Poiche' la derivata prima e' la pressione, questo e' equivalente a cercare il punto, se esiste, in cui derivata prima e seconda di  $P$  si annullano simultaneamente.

La derivata rispetto al volume, la pressione,

$$P = -\frac{\partial F}{\partial V} = \frac{Nk_B T}{V - Nb} - a \frac{N^2}{V^2} = \frac{\rho k_B T}{1 - b\rho} - a\rho^2$$

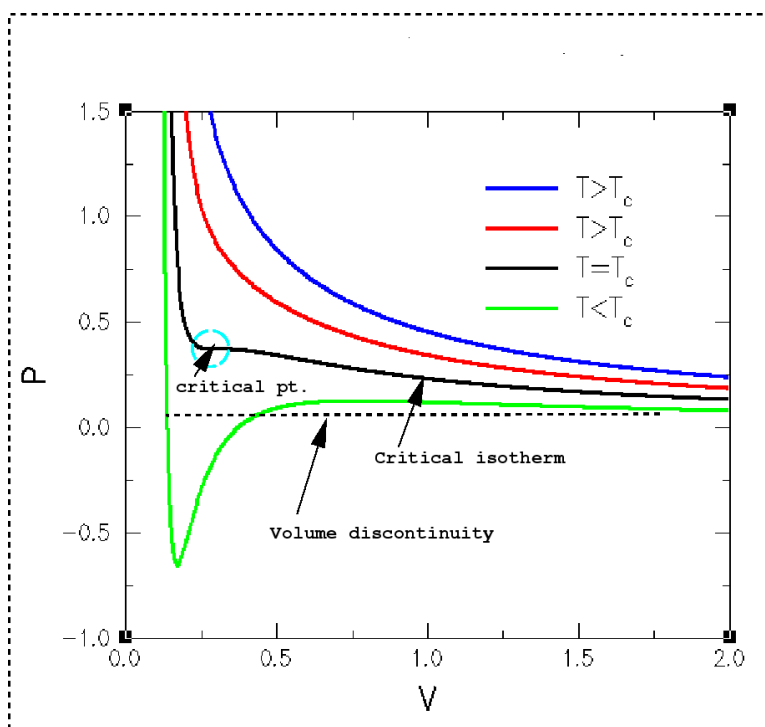
definisce l' equazione di stato di van der Waals. Notate che con questa approssimazione, abbiamo assunto che l' accensione dell' interazione attrattiva non modifica sostanzialmente la struttura spaziale del sistema di sfere dure di riferimento.

E' importante notare che l' equazione di stato  $P(V)$  assume a basse  $T$  un andamento non monotono. Infatti

$$PV^2(V - Nb) = Nk_B T V^2 - aN^2(V - Nb)$$

$$V^3P + V^2(-PNb - Nk_B T) + VaN^2 - aN^3b = 0$$

Il fatto che sia una cubica ci insegna che possono esserci od una o tre soluzioni, cioè può esistere un intervallo di temperature dove, per lo stesso valore di  $P$ , il volume può avere 3 distinti valori. Ad alta  $T$  c'è una sola soluzione (il termine di sfera dura è dominante e la pressione diverge quando  $V = Nb$ ). A bassa  $T$ , ci sono tre regioni in  $V$  distinte. Per  $V \approx Nb$ ,  $P$  diverge indipendentemente da  $T$  ed è dunque il termine dominante per piccoli volumi. Per grandi volumi  $V \gg Nb$ , il termine dominante è  $\frac{kT}{v}$ , cioè il comportamento di gas ideale. Per valori intermedi di  $V$ , specificamente per valori di  $b < V < V_{cross-over} = \frac{a}{k_B T}$ , a bassa  $T$ , il termine  $-\frac{a}{v^2}$  domina. Dunque questa espressione prevede tre soluzioni nelle isoterme di bassa temperatura.



Passando per comodità a  $\rho = N/V$  e da  $V$  a  $Nv$ , dove  $v$  è il volume per particella otteniamo

$$P = \frac{kT\rho}{1 - b\rho} - a\rho^2 = \frac{kT}{v - b} - \frac{a}{v^2}. \quad (9)$$

Calcoliamo ora il punto critico, cioè il punto dove derivata prima e seconda, a  $T$  costante, si annullano.

Poiche'

$$\frac{\partial P}{\partial v} = -\frac{kT}{(v-b)^2} + \frac{2a}{v^3} \quad (10)$$

e

$$\frac{\partial^2 P}{\partial v^2} = +\frac{2kT}{(v-b)^3} - \frac{6a}{v^4} \quad (11)$$

Imponendo che a  $T_c, P_c, v_c$  entrambe le derivate si annullino abbiamo (da  $\partial^2 P/\partial v^2 = 0$ )

$$+\frac{2kT_c}{(v_c-b)^3} - \frac{6a}{v_c^4} = 0 \quad (12)$$

con (da  $\partial P/\partial v = 0$ )

$$\frac{kT_c}{(v_c-b)^2} = \frac{2a}{v_c^3} \quad (13)$$

Si ha cosi'

$$\frac{2}{v_c-b} = \frac{3}{v_c} \quad (14)$$

da cui

$$v_c = 3b \quad (15)$$

Sostituendo si trova facilmente

$$kT_c = \frac{8}{27} \frac{a}{b} \quad (16)$$

e

$$P_c = \frac{1}{27} \frac{a}{b^2} \quad (17)$$

E' possibile utilizzare questi valori per scrivere una forma ridotta della equazione di vdW, che chiarisce la possibilita' di stati corrispondenti. Definendo  $\pi = P/P_c$ ,  $\phi = V/V_c$  e  $\theta = T/T_c$ , si trova

$$\pi P_c = \frac{\theta k_B T_c}{(\phi v_c - b)} - \frac{a}{\phi^2 v_c^2} \quad (18)$$

$$\pi \frac{1}{27} \frac{a}{b^2} = \frac{\theta \frac{8}{27} \frac{a}{b}}{(\phi 3b - b)} - \frac{a}{\phi^2 9b^2} \quad (19)$$

$$\pi = \frac{8\theta}{(3\phi - 1)} - \frac{3}{\phi^2} \quad (20)$$

$$(\pi + 3/\phi^2)(3\phi - 1) = 8\theta \quad (21)$$

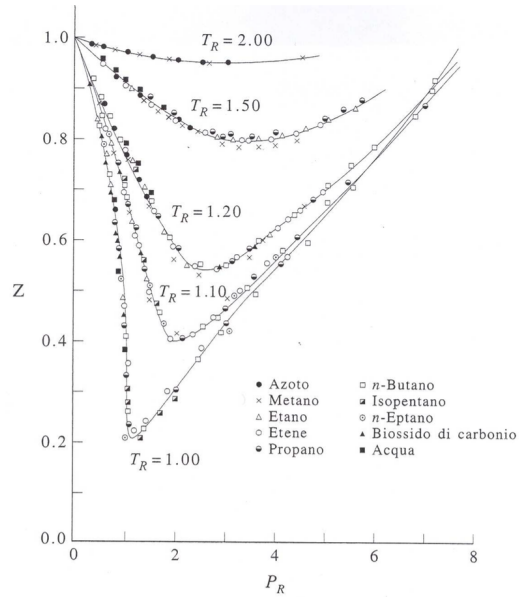
La figura seguente mostra, per alcuni gas reali, il fattore di compressibilita'  $Z^c \equiv \beta P/\rho$  a varie temperature ridotte  $\theta$  ( $Z^c$  non va confusa con la funzione di partizione). Gas diversi



si dispongono sulle stesse curve, una volta che le loro pressioni, densità e temperature sono scalate dai corrispondenti valori al punto critico. Questo collasso di dati è previsto dall'equazione di van der Waals. Infatti

$$Z^c = \frac{\beta P}{\rho} = \frac{1}{1 - b\rho} - a \frac{\rho}{kT} = \frac{1}{1 - \frac{3b}{3v}} - \frac{27kT_c b}{8} \frac{\rho}{kT} = \frac{1}{1 - \frac{1}{3\phi}} - \frac{9}{8} \frac{1}{\phi\theta}$$

$Z^c$  è dunque solo funzione di 2 variabili scalate, che tramite l'equazione di stato possono essere scelte come  $\theta, \phi, \theta, \pi, \pi, \phi$ . Nella figura che segue si è scelto di mostrare  $Z^c$  in funzione di  $\pi$  per vari valori di  $\theta$ .



## 5 How to interpret the free-energy profiles

The presence of a region of negative concavity in the free energy indicates thermodynamic instability. Indeed, as we will discuss in this section, a phase-separated system, with the same total volume and the same total number of particles has a lower free energy than the homogeneous system.

First of all we recall the conditions for coexistence. Coexistence between two phases of the same system (i.e. a condition in which atoms or molecules can freely choose in which phase to stay) requires that both phases have the same pressure (else there would be a change in volume in the two phases), the same temperature (else there would be heat flux between the two phases) and the same chemical potential (else particles would migrate from one phase to the other)

$$P_{phaseI} = P_{phaseII} \quad (22)$$

$$T_{phaseI} = T_{phaseII} \quad (23)$$

$$\mu_{phaseI}(P, T) = \mu_{phaseII}(P, T) \quad (24)$$

The chemical potential  $\mu \equiv G/N$  is the Gibbs free energy ( $G = F + PV = U - TS + PV$ ) per particle. Indeed,  $G$  is a function of  $P$  and  $T$ . It must also be extensive. Hence  $G = Nf(P, T)$ . So  $\mu = \partial G / \partial N = f(P, T) = G/N$ .

At coexistence  $\Delta\mu \equiv \mu_{phaseI}(P, T) - \mu_{phaseII}(P, T) = 0$  and hence (retaining the meaning of  $\Delta$  as the difference between the two coexisting phases

$$\Delta\mu = \frac{\Delta(F + PV)}{N} = \frac{\Delta U - T\Delta S + P\Delta V}{N} = 0$$

such that

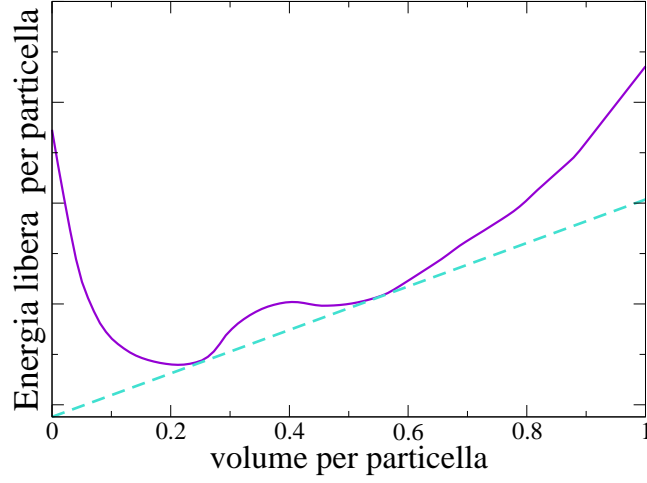
$$\Delta h \equiv \frac{\Delta U + P\Delta V}{N} = T\Delta s \equiv T \frac{\Delta S}{N}$$

To select the two coexisting phases from the knowledge of  $F(V, T)$  it is sufficient to plot the volume dependence of  $F$  along an isotherm and see if there are conditions such that a common tangent line, simultaneously tangent to more than one point can be drawn. The two tangent points have indeed the same  $T$  by construction (isotherm) and the same  $P$  since the slope of the tangent line is indeed the pressure  $P$  ( $P = -\frac{\partial F}{\partial V}|_T$ ). The same two points have also the same chemical potential. Indeed they share not only the slope but also the intercept  $F_0$  of the common tangent line. Hence for both points (being  $-P$  the slope)

$$F(V_I) = F_0 - PV_I \quad F(V_{II}) = F_0 - PV_{II}$$

such that

$$F(V_I) + PV_I = F(V_{II}) + PV_{II} \quad \rightarrow \quad G(V_I) = G(V_{II}) \quad \text{or} \quad \mu_I = \mu_{II}$$



Finally, let's check that the free energy of the phase separated sample is lower than the free energy of the homogeneous sample with the same average density.

The two conditions that must be satisfied are

$$Nv = N_1v_1 + N_2v_2$$

and

$$N = N_1 + N_2$$

where  $N_1$  and  $N_2$  are the number of molecules in the two phases and  $v_1$  and  $v_2$  are the volumes per particle in the two coexisting phases. Then

$$N_1 = N - N_2 \quad Nv = (N - N_2)v_1 + N_2v_2 = Nv_1 + N_2(v_2 - v_1)$$

or

$$N_2 = N \frac{v - v_1}{v_2 - v_1} \quad \text{and} \quad N_1 = N \frac{v - v_2}{v_1 - v_2}$$

As a result the system free energy is (neglecting the interfacial energy)

$$Nf = N_1f_1 + N_2f_2 = Nf_1 \frac{v - v_2}{v_1 - v_2} + Nf_2 \frac{v - v_1}{v_2 - v_1} = N \frac{f_1(v - v_2) - f_2(v - v_1)}{v_1 - v_2} =$$

$$f = \frac{(f_1 - f_2)v - (f_1v_2 - f_2v_1)}{v_1 - v_2} = \frac{(f_1 - f_2)}{v_1 - v_2}v - \frac{(f_1v_2 - f_2v_1)}{v_1 - v_2}$$

e.g. exactly the straight line passing through  $v_1$  and  $v_2$  with the slope equal to the pressure  $\frac{f_2 - f_1}{v_2 - v_1}$

The lesson to learn is then that as soon as the volume dependence of the Helmholtz free energy has a non concave shape (such that a common tangent line can be drawn, than there exist a region of volumes for which the stable thermodynamic state is composed by two coexisting phases.

### 5.0.1 How to calculate coexistence (Maxwell rule)

We have seen that coexistence between two phases requires equality of  $T$ ,  $P$  and  $\mu$ . This requires that

$$(F + PV)_1 = (F + PV)_2$$

or equivalently

$$P(V_2 - V_1) = F_1 - F_2$$

Since

$$P = -\left.\frac{\partial F}{\partial V}\right|_T$$

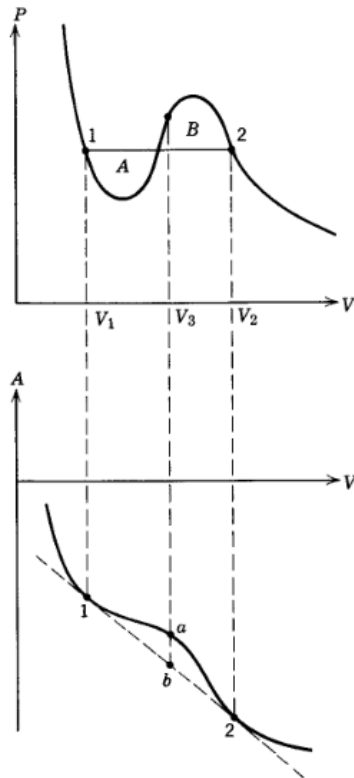
by integrating along an isotherm

$$F(V, T) = F(V_0, T) - \int_{V_0}^V P dV$$

the equal  $\mu$  condition becomes

$$P(V_2 - V_1) = F_1 - F_2 = \int_{V_1}^{V_2} P dV$$

The left side is the surface of a rectangle and hence one can conclude that the phase coexistence can be equivalently expressed as equal areas between the EOS and the coexisting pressure.



**Fig. 2.11** The Maxwell construction.

## 6 Difference between metastable and unstable

In the unstable region, we can still discriminate between metastable and truly unstable state points. While the difference is properly defined only in mean-field, far from the spinodal point it retains some validity (and indeed explains the experimentally observed supercooled and stretched states).

One simple way to see why there is a difference is to try to repeat the same argument developed to determine the system free energy at a local scale. For the sake of understanding, let's consider an homogeneous system in the unstable region and imagine that a fluctuation locally increases the density at the expenses of the density in nearby regions. Let's assume that  $v_1$  and  $v_2$  are this time the volume per particle in the denser and less dense regions just generated. Then, using the same argument as before, the system free energy can be expressed as

$$f(v) = \frac{(f_1 - f_2)v - (f_1v_2 - f_2v_1)}{v_1 - v_2} = \frac{(f_1 - f_2)}{v_1 - v_2}v - \frac{(f_1v_2 - f_2v_1)}{v_1 - v_2}$$

This equation is once more the line connecting  $v_1$  and  $v_2$ . In the concave region, this line is

above the free-energy profile, while in the convex region, it is below. This suggests that in the concave region, a microscopic change in density requires an increase in the overall free-energy (e.g. the existence of a free-energy barrier for nucleating the stable phases), while in the convex region — no matter how small the fluctuation is — the free-energy will always be lower. Hence there are no barrier and the phase-separation process is immediately active.

## 6.1 The spinodal for vdW

Una quantita' utile per definire il limite di stabilita' dello stato liquido in campo medio e' data dalla cosi-detta curva spinodale, definita da  $\partial\pi/\partial\phi = 0$ . Nel caso di vdW,

$$\frac{-24\theta}{(3\phi - 1)^2} + \frac{6}{\phi^3} = 0 \quad (25)$$

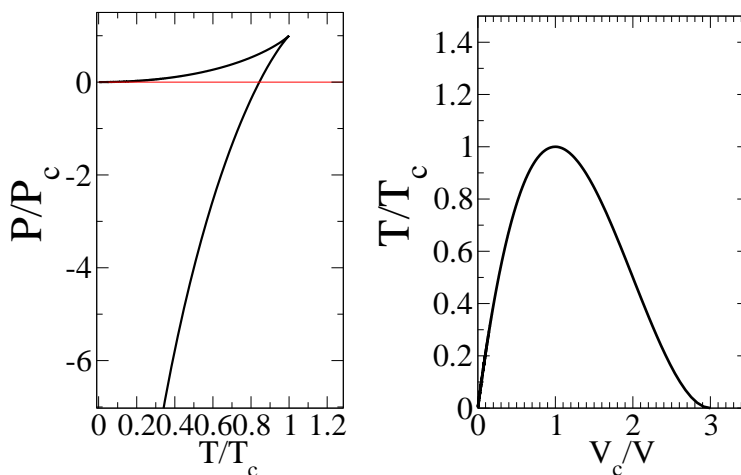
che fornisce una relazione tra  $\theta$  e due distinti valori di  $\phi$  lungo la curva spinodale.

$$\theta_s = \frac{(3\phi_s - 1)^2}{4\phi_s^3} \quad (26)$$

A  $\theta_s = 0$ , i due valori sono rispettivamente il valore di close-packing secondo vdW ( $\phi = 1/3$ ) e  $\phi = 0$  (gas ideale).

Inserendo  $\theta_s$  e  $\phi_s$  nella equazione di stato (Eq.21) otteniamo la pressione spinodale.

La curva spinodale nel piano  $\pi, \theta$  e'



$$\pi_s = \frac{3\phi_s - 2}{\phi_s^3} \quad (27)$$

E' interessante notare che  $\pi_s$  diviene negativo, suggerendo che il liquido di vdW e' capace di sopportare pressioni negative (in equilibrio metastabile). Esiste anche un limite alla massima pressione negativa sostenibile dal liquido, per  $\theta = 0$ . In questo caso,  $\phi_s = 1/3$  e  $\pi_s = -27$ .

## 6.2 The spinodal for the lattice-gas

The spinodal for the lattice gas is easily found by solving the equation

$$\frac{d^2 \beta f}{d\phi^2} = 0$$

corresponding (close to  $T_c$ , having used the expansion)

$$4 \left( 1 - \frac{T_c}{T_{spinodal}} \right) + 16(\phi_{spinodal} - \phi_c)^2 = 0$$

The full solution shows that  $\phi_{spinodal} \rightarrow 0, 1$  when  $T_{spinodal} \rightarrow 0$ .

## 7 Density fluctuations diverge at the critical point

Let's go back to the van der Waals EOS, expressed in scaled units ( $P_c, T_c, V_c$ , all equals to 1)

$$P = \frac{8T}{3V-1} - \frac{3}{V^2}$$

The isothermal compressibility is defined as

$$k_T = -\frac{1}{V} \frac{\partial V}{\partial P} \Big|_T$$

The derivative  $\frac{\partial P}{\partial V} \Big|_T$  (note the inverse) is easily calculated from the EOS as

$$\frac{\partial P}{\partial V} \Big|_T = 8T \frac{-3V}{(3V-1)^2} + \frac{6}{V^2}$$

Then, along the critical isochore,  $V = 1$ .

$$k_T = \left( -V \frac{\partial P}{\partial V} \Big|_T \right)^{-1} = \left( \frac{-3}{4} 8T + 6 \right)^{-1} = [6(1-T)]^{-1} \quad (28)$$

and hence  $k_T$  diverges with a (mean field) critical exponent  $\gamma = -1$ .

## 7.1 Scaling of the order parameter (distance from the critical volume) along the coexistence curve

Se espandiamo la equazione di stato intorno al punto critico,

$$P = \frac{8T}{3V-1} - \frac{3}{V^2} = \frac{8T-8+8}{3V-3+3-1} - \frac{3}{(V-1+1)^2} = \frac{8(T-1)+8}{3(V-1)+2} - \frac{3}{[(V-1)+1]^2}$$

troviamo (utilizzando

$$\frac{1}{3x+2} = \frac{1}{2} \left[ 1 - \frac{3}{2}x + \frac{9}{4}x^2 - \frac{27}{8}x^3 \right] \quad \text{e} \quad -\frac{3}{(1+x)^2} = -3 [1 - 2x + 3x^2 - 4x^3]$$

$$P = 1 - \frac{3(V-1)^3}{2} + (T-1) \left( -\frac{27(V-1)^3}{2} + 9(V-1)^2 - 6(V-1) + 4 \right)$$

Se assumiamo (e lo mostreremo dopo) che  $O(V-1)^2 \sim O((T-1))$ , possiamo semplificare

$$P = 1 - \frac{3(V-1)^3}{2} + 4(T-1) - 6(T-1)(V-1)$$

che costituisce una espressione dell' equazione di stato vicino al punto critico. Quando  $P = 1 + 4(T-1)$ ,  $V = 1$  e' soluzione. Per lo stesso valore di  $P$  e  $T$  esistono anche come soluzioni

$$-\frac{3(V-1)^3}{2} - 6(T-1)(V-1) = 0$$

cioe'

$$(V-1)^2 = -4(T-1) \quad V_{1,2} = 1 \pm \sqrt{4(1-T)}$$

cioe' due soluzioni simmetriche rispetto a  $V = 1$ . Chiamiamo  $1 + 4(T-1) = P_{coex}$ . Infatti per questo valore di  $P$  e  $T$ ,

$$\int_{V_1}^{V_2} (P - P_{coex}) dV = \left[ -\frac{3(V-1)^4}{8} - 3(T-1)(V-1)^2 \right]_{V_1}^{V_2} = 0$$

Dunque

$$\frac{V - V_c}{V_c} = 4 \sqrt{\frac{T_c - T}{T_c}}$$

che mostra che il parametro d' ordine  $V - V_c$  scala con  $|T - T_c|$  con un esponente critico  $1/2$ .



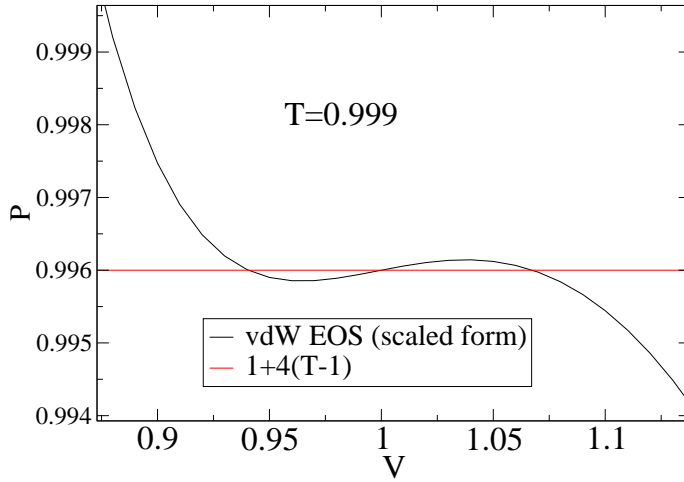


Figure 1: vdW vicino al punto critico ( $T/T_c = 0.999$ )

### 7.1.1 Scaling a $T_c$

Abbiamo visto che

$$P = 1 - \frac{3(V-1)^3}{2} + 4(T-1) - 6(T-1)(V-1)$$

e dunque a  $T = 1$ ,

$$P - 1 = -\frac{3(V-1)^3}{2}$$

per cui

$$\frac{V - V_c}{V_c} \sim \left( \frac{P - P_c}{V_c} \right)^{1/3}$$

## 7.2 Esponenti Critici

Se confrontiamo il comportamento della teoria di van der Waals e di una qualsiasi delle teorie qui sviluppate per il modello di Ising scopriamo che si manifesta un comportamento uguale vicino al punto critico. Identificando come parametro d'ordine la differenza di densità nel caso del fluido e la magnetizzazione nel caso di Ising in entrambi i casi, chiamando  $\epsilon \equiv (T - T_c)/T_c$ ,

$$L(T) \sim (-\epsilon)^\beta \quad \rho - \rho_c = (-\epsilon)^\beta \quad \beta = 0.5$$

e

$$\left(\frac{\partial \bar{L}}{\partial H}\right)_{H=0} \sim |\epsilon|^{-\gamma} \quad \frac{1}{V} \frac{\partial V}{\partial P} \sim |\epsilon|^{-\gamma} \quad \gamma = 1$$

Infine, se guardiamo com varia il parametro d' ordine con il campo esterno

$$L(H) \sim H^{1/\delta} \quad \rho - \rho_c \sim (P - P_c)^{1/\delta} \quad \delta = 3$$

Tutti questi andamenti sono descritti quindi da leggi di potenza. Sperimentalmente si osservano effettivamente leggi di potenza ma con esponenti, universali, differenti. Specificamente  $\beta \approx 1/3$ ,  $\gamma \approx 5/4$ ,  $\delta \approx 5$ .

Il campo medio quindi ci consente di capire quello che sta succedendo, ma la descrizione dell' energia libera in vicinanza del punto critico non e' esatta. Una nuova teoria, il gruppo di rinormalizzazione, consente di predire gli esponenti corretti.

## 8 Decomposizione spinodale

To model the temporal evolution of a system instantaneously quenched from temperatures higher to temperatures lower than the critical temperature, one uses the Cahn-Hilliard equation, initially proposed for metallic alloys but of broader applicability. The equation describes the evolution of density in an inhomogeneous system, whose free energy is described as:

$$F(V, T) = \int d\mathbf{r} \left[ f_0(\rho) + k (\nabla \rho)^2 \right]$$

Here, the density  $\rho(\mathbf{r})$  is a function of space. The term involving the gradient models the energetic cost associated with the creation of interfaces.

For simplicity, let's consider the process in one dimension, but similar results are obtained in three dimensions.

$$F = \int dx \left[ f_0(\rho) + k \left( \frac{d\rho}{dx} \right)^2 \right]$$

The fact that the density is not constant leads to a spatial variation in the chemical potential, and hence, a flow of matter proportional to the gradient of  $\mu$ . Indeed the flux  $J$  is

$$J = -M \frac{d\mu}{dx}$$

where  $M$  is a (positive) transport coefficient that we assume to be independent of  $\rho$ . The chemical potential is related to the free energy by the equation

$$\mu = \frac{\partial F}{\partial N} \Big|_T = \frac{1}{V} \frac{\partial F}{\partial \rho} \Big|_T$$

The chemical potential is thus a functional derivative of  $F$  with respect to  $\rho$ . To evaluate it, let's see how  $\delta F$  changes

$$\delta F = \int dx \left[ f_0(\rho + \delta\rho) + k \left( \frac{d(\rho + \delta\rho)}{dx} \right)^2 - f_0(\rho) - k \left( \frac{d\rho}{dx} \right)^2 \right]$$

da cui

$$\delta F = \int dx \left[ f_0(\rho) + f_0'(\rho)\delta\rho + k \left( \frac{d\rho}{dx} \right)^2 + k \left( \frac{d(\delta\rho)}{dx} \right)^2 + 2k \left( \frac{d\rho}{dx} \frac{d\delta\rho}{dx} \right) - f_0(\rho) - k \left( \frac{d\rho}{dx} \right)^2 \right]$$

e al primo ordine in  $\delta\rho$

$$\delta F = \int dx \left[ f_0'(\rho)\delta\rho + 2k \left( \frac{d\rho}{dx} \frac{d\delta\rho}{dx} \right) \right]$$

Integrando per parti il secondo integrale

$$\delta F = \int dx \left[ f_0'(\rho)\delta\rho - 2k \frac{d^2\rho}{dx^2} \delta\rho \right] - 2k \frac{d\rho}{dx} \delta\rho \Big|_{-\infty}^{\infty}$$

per cui

$$\mu(x) = \frac{\delta F}{\delta\rho} = f_0'(\rho) - 2k \frac{d^2\rho}{dx^2}$$

Il flusso associato e' dunque

$$J = -M \frac{d\mu}{dx} = -M \left( f_0''(\rho) \frac{d\rho}{dx} - 2k \frac{d^3\rho}{dx^3} \right)$$

Dalla equazione di continuita

$$\frac{d\rho}{dt} = - \frac{dJ}{dx}$$

otteniamo (nella approssimazione di piccole variazioni di densita, così da trascurare la dipendenza dalla densita di  $f_0''(\rho)$ )

$$\frac{\partial\rho}{\partial t} = M \left( f_0'' \frac{\partial^2\rho}{\partial x^2} - 2k \frac{\partial^4\rho}{\partial x^4} \right)$$

If  $k$  were zero and the system were stable ( $(f_0'' > 0)$ ), this equation would describe the standard diffusion process, which leads to the homogenization of density in the presence of initial inhomogeneities, with a diffusion coefficient  $D$  equal to  $Mf_0''$

The spatial Fourier transform allows us to write:

$$\frac{\partial \rho_q}{\partial t} = -M f_0'' \rho_q q^2 - 2k M \rho_q q^4$$

da cui

$$\rho_q(t) = \rho_q(0) e^{M f_0'' q^2 t \left(-1 - \frac{2k}{f_0''} q^2\right)}$$

Questa equazione mostra che, poichè dentro la zona spinodale  $f_0'' = -|f_0''| < 0$ ,

$$\rho_q(t) = \rho_q(0) e^{-M |f_0''| q^2 t \left(-1 + \frac{2k}{|f_0''|} q^2\right)}$$

e le fluttuazioni di densità presenti al tempo zero decadono quando

$$\left(-1 + \frac{2k}{|f_0''|} q^2\right) > 0$$

cioè solo per

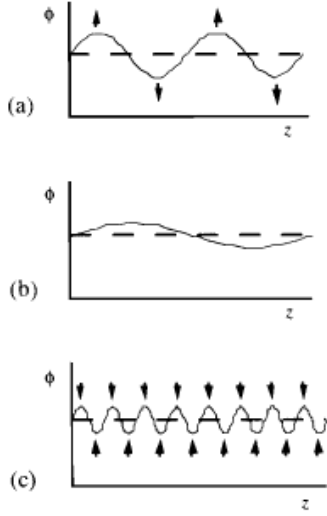
$$q^2 > \frac{|f_0''|}{2k}$$

Inoltre, c'è un vettore d'onda specifico al quale le fluttuazioni hanno massima rapidità di crescita. Derivando l'argomento dell'esponenziale ed uguagliandolo a zero per trovare gli estremi abbiamo

$$\frac{d \left[ q^2 \left( -1 + \frac{k}{|f_0''|} q^2 \right) \right]}{dq} = -2q + 4 \frac{2k}{|f_0''|} q^3 = 2q \left[ -1 + 2 \frac{2k}{|f_0''|} q^2 \right] = 0$$

che ha come soluzione  $q = 0$  e

$$q_{max} = \left[ \frac{|f_0''|}{4k} \right]^{\frac{1}{2}}$$



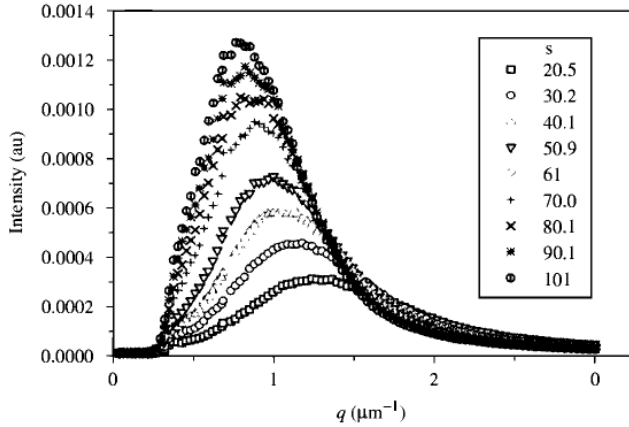
**Fig. 3.7** Why concentration fluctuations of one particular intermediate length scale grow fastest in spinodal decomposition. In (b), a long-wavelength fluctuation grows relatively slowly, as the distances material has to diffuse from troughs to peaks are relatively large. In (c), too much new interface is created, with a correspondingly large free energy penalty; these fluctuations do not grow at all. An intermediate length scale (a) grows the fastest and dominates the pattern of phase separation.

So, there is a wave vector,  $q_{max}$ , at which the rate of growth of density fluctuations is maximum. In the linear region, the structure factor will exhibit a peak at  $q_{max}$  that grows exponentially over time.

$$S(q, t) = |\rho_q(t)|^2 = S(q, 0) e^{-2M|f_0''|q^2 t \left( -1 + \frac{2k}{|f_0''|} q^2 \right)}$$

Let's also note that during the process of spinodal decomposition, diffusion occurs from regions with lower concentration to regions with higher concentration. In such cases, it's referred to as negative diffusion.

After the linear region, the absolute value of density continues to increase (until it reaches the coexistence value) and then remains constant. Meanwhile, the so-called "coarsening" process begins, during which the maximum wave vector,  $q_{max}$ ?, progressively decreases over time. This process is now guided by the reduction of interfaces and continues until the system has macroscopically separated into two phases. In the absence of gravity, this process can take extremely long times.



**Fig. 3.10** Light-scattering curves from a polymer mixture quenched into the unstable region of the phase diagram, showing the maximum in intensity at  $q_{\max}$  characteristic of spinodal decomposition.  $q_{\max}$  moves to smaller values at longer annealing times, owing to non-linear coarsening effects. Graph courtesy of B. Jung.

For a graphical solution of the Cahn-Hilliard equation see for example [click here](#)

## 9 Colloidal and biological phenomena related to phase separation

- Protein phase diagrams
- Colloidal gelation
- Membran less organelles
- Hard Spheres (first order phase transitions)