

# Lecture 9

## *Kinetics of Type I Phase Transitions.*

### *Nucleation and Coalescence.*

Studying the kinetics of the type I phase transitions, i.e. the dynamics of the growth of a thermodynamically more advantageous phase within the less advantageous one, we come across several problems, of which we will examine two: nucleation and coalescence.

#### **Type I Phase Transition. Transition Line.**

Consider the condensation of a liquid from an over-saturated vapour. It is known that the phase equilibrium occurs on the line  $T_t(p)$  in the  $p-T$  plane. On this line, the molar free energies of vapour and liquid coincide,  $F_l(T, p) = F_v(T, p)$ . This gives

$$-S_l dT + v_l dp = -S_v dT + v_v dp, \quad (1)$$

where  $S_i$  and  $v_i$  are the molar entropy and the molar volume respectively in both of the phases. Equation (1) leads to the Clapeyron-Clausius equation for the line of the phase transition:

$$\frac{d}{dp}T_t(p) = \frac{\Delta v}{\Delta S} = T \frac{\Delta v}{\lambda}, \quad (2)$$

where  $\Delta v = v_v - v_l$  is the difference in molar volumes in vapor and liquid and  $\lambda$  is the latent heat of evaporation. If evaporation occurs at temperatures much lower, than the critical temperature, then the volume of liquid is negligible, while the volume of vapour phase obeys the law

$$v_v p = RT.$$

This gives, approximately,

$$p_t(T) \propto \exp \left[ - \frac{\lambda}{RT} \right]. \quad (3)$$

Thus, liquid and vapour have equal free energies at the transition line. On both sides of this line, either liquid or vapour are advantageous as the bulk thermodynamic phases. Nevertheless, the less advantageous phase (say, vapour) remains stable by itself (meta-stable). Moreover, we will see that the process of transition is considerably hindered.

The transition of vapour into liquid goes through formation of small droplets. The formation of a droplet of radius  $a$  leads to the energy gain  $-(4\pi a^3/3) \Delta F$  due to the difference in the bulk free energies ( $\Delta F = F_v - F_l > 0$ ) and to the disadvantage of creating a surface  $4\pi\alpha a^2$ , where  $\alpha$  is the surface energy. Fig 1 shows that total energy of formation of a droplet versus its radius  $a$ . One can see a potential barrier of the height  $F_c = (16\pi/3)\alpha^3/(\Delta F)^2$  at the the critical

radius  $a_c = 2\alpha/\Delta F$ . The closer we are to the transition line (small  $\Delta F$ ), the larger is the critical radius, and the higher is the barrier. The droplets of a small radius  $a < a_c$  are unstable with respect to collapse. The droplets of a large radius  $a > a_c$  are also unstable: they grow and with their growth the vapour phase is replaced the liquid one.

Therefore, the process of condensation of an over-saturated vapour begins with nucleation of the droplets of the critical radius  $a_c$ . After a considerable amount of vapour is transformed into these droplets, the over-saturation drops down. This makes the nucleation of new droplets very unprobable, and the nucleation is substituted by the coales-

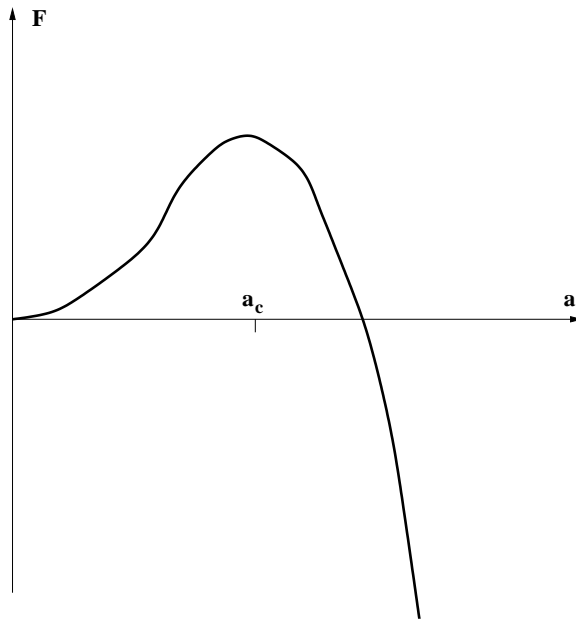


Figure 1: Free energy of a droplet in a vapor as a function of its radius  $a$

cence, i.e. growth of already existing droplets.

## Nucleation

The distribution function  $f(a, t)$  of droplets in their size  $a$  varies in time because the droplets of over-critical size  $a > a_c$  continue to grow, while the droplets of under-critical size  $a < a_c$  experience two trends: they are collapsing due to surface pressure and grow due to fluctuational condensation of vapour on them. The quasi-equilibrium distribution function

$$f_0(a) = \exp \left[ - \frac{F(a)}{T} \right], \quad F(a) = - \frac{8\pi\alpha a^3}{3a_c^3} + 4\pi\alpha a^2 \quad (4)$$

gives the thermal fluctuation driven “equilibrium” distribution of the droplets. Near the top of the barrier, the free energy  $F(a)$  may be expanded to second order in  $a - a_c$ :

$$F(a) \approx \frac{4\pi\alpha a_c^3}{3} - 4\pi\alpha(a - a_c)^2, \quad (5)$$

so that the distribution functions  $f_0(a)$  is approximately equal to:

$$f_0(a) = f_0(a_c) \exp \left[ \frac{4\pi\alpha(a - a_c)^2}{T} \right] \quad (6)$$

$$f_0(a_c) = \exp \left[ - \frac{4\pi\alpha a_c^3}{3T} \right]. \quad (7)$$

Equation (7) gives (to the exponential precision) the amount of droplets which have reached the critical size and may

grow further, or the rate of nucleation. The purpose of the kinetic theory is to calculate the pre-exponential factor. The process of the droplet's growth (or collapse) involves molecules of the vapor condensing at the droplet (evaporating from it) as a result of their thermal motion. Since this is a very gradual process, the distribution function  $f(a, t)$  obeys the Fokker-Plank equation:

$$\frac{\partial f}{\partial t} + \frac{\partial s}{\partial a} = 0; \quad s = -B \left( \frac{\partial f}{\partial a} + f \frac{F(a)}{T} \right), \quad (8)$$

where a new kinetic coefficient  $B$  has the meaning of the coefficient of diffusion in sizes of droplets. The boundary conditions Eq (8) are:

$$\frac{f(a)}{f_0(a)} = 1, \quad \text{at } a \rightarrow 0; \quad \frac{f(a)}{f_0(a)} = 0, \quad \text{at } a \rightarrow \infty. \quad (9)$$

Stationary nucleation corresponds to a constant flux  $s$ , which itself may be expressed through the ratio  $f(a)/f_0(a)$ :

$$s = -B f_0 \frac{\partial}{\partial a} \frac{f}{f_0}. \quad (10)$$

Equation (10) gives

$$\frac{f(a)}{f_0(a)} = -s \int \frac{da}{B f_0(a)}, \quad (11)$$

where the limits of integration should be found from the boundary conditions (9):

$$\frac{f(a)}{f_0(a)} = -s \int_a^\infty \frac{da}{B f_0(a)}, \quad \frac{1}{s} = \int_0^\infty \frac{da}{B f_0(a)}. \quad (12)$$

Since the integrand in Eq (12) has a strong maximum at  $a = a_c$ , the region near it determines the value of the flux which can be found from the boundary conditions (9):

$$s = 2\sqrt{\frac{\alpha}{T}} B(a_c)f_0(a_c) \quad (13)$$

Equation (10) gives the rate of nucleation per unit volume and unit time. As it has been mentioned, this rate is exponentially small for small over-saturation of the vapour and the pre-exponential factor is determined by the coefficients of “diffusion” in radii  $B$  for the critical radius  $a_c$  and the distribution width  $\delta a = (4\pi\alpha/T)^{1/2}$  caused the by thermal fluctuations.

## Coalescence

As it has been mentioned, nucleation occurs only at the initial stage of transition. When the amount of droplets exceeds a certain limit, the process of coalescence of existing droplets prevails over nucleation. The distribution function  $f(a, t)$  still obeys the Fokker-Planck type equation (8), in which the diffusion-like term may be omitted:

$$\frac{\partial f}{\partial t} + \frac{\partial}{\partial a} (\dot{a} f) = 0. \quad (14)$$

Having in mind the condensation of the water vapour in air, let's determine the kinetic coefficient  $\dot{a}$  (or, equivalently,  $B$  of the previous section). If the centre of the droplet of

radius  $a$  is at the origin and the equilibrium concentration of the vapor in air far away from the droplet is  $c_\infty$ , then the equilibrium concentration  $c_0$  at the surface of the droplet differs from  $c_\infty$  due to Laplace's surface pressure and is equal to:

$$c_0 = c_\infty \left( 1 + \frac{2\alpha}{T a c_w} \right), \quad (15)$$

where  $c_w$  is the molar density of water.

The growth of the droplet occurs due to the diffusion of the vapour from infinity to the droplet. The stationary solution of the diffusion equation,

$$D \nabla^2 c(\mathbf{r}) = 0,$$

which depends on radius only, has the form

$$c(r) = c - (c - c_0) \frac{a}{r}.$$

The growth of the droplet's volume,  $\dot{V} = 4\pi a^2 \dot{a}$ , is determined by the diffusion flux  $j = 4\pi a^2 D (dc/dr)_{r=a}$  multiplied by the ratio of molar concentrations  $c_w/c$ :

$$\dot{a} = \frac{Dc}{c_w} \frac{c - c_0}{a} = \frac{Dc}{c_w} \frac{1}{a} \left( \Delta - \frac{\sigma}{a} \right), \quad (16)$$

where

$$\sigma = \frac{2\alpha c_\infty}{T c_w}$$

and  $\Delta = c - c_\infty$  is over-saturation of air by vapour. The value

$$a_c(t) = \frac{\sigma}{\Delta(t)} \quad (17)$$

is the critical radius of the droplet (in the sense of nucleation) for the given over-saturation  $\Delta(t)$  which itself depends on time. Thus, coalescence begins at time  $t = 0$  with a certain over-saturation  $\Delta(0)$ , when the critical radius is equal to  $a_c(0)$ . The radius of droplets change with time<sup>1</sup>, obeying the equation of growth:

$$\dot{a} = \frac{a_c^3(0)}{a} \left( \frac{1}{a_c(t)} - \frac{1}{a} \right). \quad (18)$$

If the total initial over-saturation is  $Q$ , then the over-saturation at a given time diminishes with time, and more and more vapour condenses into droplets:

$$\Delta(t) + q(t) = Q, \quad q(t) = \frac{4\pi c_w}{3 c_\infty} \int_0^\infty f(a, t) a^3 da. \quad (19)$$

Now we have to solve Eqs (14) and (18) with the constraint (19). It is natural to use the variable

$$u = \frac{a}{a_c(t)}$$

instead of the droplet's radius  $a$  and an implicit time  $x = a_c(t)/a_c(0)$  instead of the explicit time  $t$ . It is even more convenient to use the logarithmic time

$$\tau = 3 \ln x(t).$$

After all these substitutions, the growth equation (18) takes the following form:

$$\frac{du^3}{d\tau} = \Phi(u) = \gamma(\tau)(u - 1) - u^3, \quad \gamma(\tau) = \frac{dt}{x^2 dx} > 0. \quad (20)$$

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<sup>1</sup>From now on, until the formulation of the final results, we will measure time in the units of  $a_c^3(0)c_w/Dc_\infty\sigma$



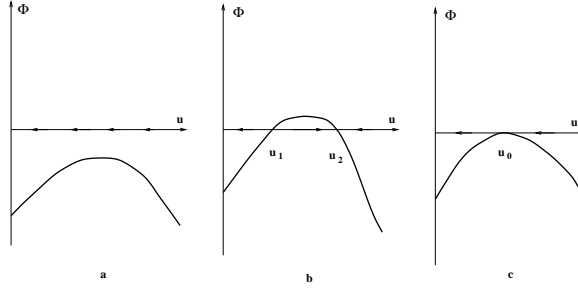


Figure 2: The growth function  $\Phi(u)$  of a droplet as a function of its radius  $u$

At any given time  $\tau$ , the right hand side of Eq (20) has a maximum at  $u_0^2 = \gamma/3$  and

$$\Phi(u_0) = \gamma \left[ \frac{2}{3} \left( \frac{\gamma}{3} \right)^{1/2} - 1 \right].$$

Therefore, depending on the value of  $\gamma$ , the function  $\Phi(u)$  either has two zeros, or one double zero, or no zeros at all and  $\Phi(u) < 0$  (see Fig 2). The double zero occurs if  $\Phi(u_0) = 0$ , i.e. for  $\gamma = \gamma_0 = 27/4$ .

For  $\gamma < \gamma_0$  the function  $\Phi(u)$  is negative for all  $u > 0$  (see Fig 2, a ). This means that irrespective of the initial condition for Eq (20),  $u = 0$  at some finite time  $\tau$ . At this time,  $q(t) = 0$  contrary to the basic assumption. Therefore, this may not be true.

For  $\gamma > \gamma_0$  the function  $\Phi(u)$  has two zeros,  $u_1 < u_2$ , and is negative if  $u > u_2$  and  $u < u_1$ , and positive if  $u_1 < u < u_2$  (see Fig 2, b ). This means that if the initial condition belongs to the interval  $[0, u_1]$ , then the radius goes to zero in a finite time ; otherwise, it goes to  $u = u_2$ . So, the distribution function has a peak at  $a(t) = u_2 a_c(t) \rightarrow \infty$ .

This leads to the volume of the condensate  $q(t)$  growing indefinitely with time, which contradicts to the constraint (19).

In the case  $\gamma = \gamma_0$ ,  $\Phi(u) \leq 0$  with  $\Phi(u) = 0$  for  $u = u_0$  only. This leads to  $u$  evolving towards zero in a finite time if the initial condition belongs to the interval  $[0, u_0]$  and evolving towards  $u_0$  if the initial condition belongs to the interval  $[u_0, \infty]$ . Thus, if

$$\gamma(\tau) = \frac{27}{4}[1 - \epsilon^2(\tau)], \quad \epsilon(\tau)|_{\tau \rightarrow \infty} \rightarrow 0, \quad (21)$$

the evolution of the initial condition includes drift to small values of dimensionless radius  $u$  which is accompanied by a long time spent at  $u \approx u_0$ . The occupation numbers  $f(a, t)$  at  $a = ac(t)u_0$  plays the role of the initial conditions for the universal distribution for  $u < u_0$

The condition  $\gamma \approx \gamma_0 = 27/4$  gives

$$x^2 \frac{dx}{dt} \approx \frac{4}{27}, \quad x(t) = \frac{a_c(t)}{a_c(0)} \approx \left(\frac{4t}{9}\right)^{1/3}. \quad (22)$$

The last equation gives the time dependence of the critical radius for a droplet in an over-saturated vapour in air at a given time  $t \rightarrow \infty$ . For  $u \approx u_0 = 3/2$ , the equation of growth (20) takes the following form:

$$\frac{du}{d\tau} = -\frac{2}{3} \left(u - \frac{2}{3}\right)^2 - \frac{\epsilon^2}{2}. \quad (23)$$

Introducing a new variable

$$z = \frac{1}{\epsilon(\tau)} \left(u - \frac{3}{2}\right),$$

we can rewrite Eq (23) in the form

$$\frac{3}{2\epsilon} \frac{dz}{d\tau} = \Psi(z) = -z^2 - \frac{3}{4} + \frac{3}{2} z\eta, \quad (24)$$

where

$$\eta(\tau) = \frac{d}{d\tau} \left( \frac{1}{\epsilon} \right).$$

Equation (24) may be investigated in the same manner as Eq (20). Using the same reasoning, we arrive at the conclusion that  $\Psi(z) \leq 0$ . Completed the square in the right-hand side of Eq (24) ( $\Psi(z) = -(z - 1/2\sqrt{3})^2$ ), we see that the  $\Psi(1/2\sqrt{3}) = 0$  at  $\eta = 2/\sqrt{3}$ . Therefore, the limit of the function  $\eta(\tau)$  as  $\tau \rightarrow \infty$  is  $\eta = \eta_0 = 2/\sqrt{3}$ . This gives the asymptote for  $\epsilon(\tau)$ :

$$\epsilon(\tau) = \frac{\sqrt{3}}{2\tau}. \quad (25)$$

The asymptotic distribution of droplets in their radii  $a$  may be obtained as a solution of the Fokker-Planck equation (14). The distribution function  $\phi(u, t) = f(a, t)/a_c(t)$  in dimensionless variables  $u$  and  $\tau$  obeys the equation:

$$\frac{\partial \phi}{\partial \tau} + \frac{\partial}{\partial u} (\dot{u} \phi) = 0, \quad (26)$$

$$\dot{u}(u) = \frac{du}{d\tau} = -\frac{1}{3u^2} \left( u - \frac{2}{3} \right)^2 (u + 3). \quad (27)$$

The solution of Eq (26) has the form

$$\phi(u, \tau) = \frac{\chi[\tau - \tau(u)]}{-\dot{u}(u)}, \quad \tau(u) = \int_0^u \frac{du'}{\dot{u}(u')}. \quad (28)$$

where  $\chi$  is an arbitrary function of its argument. The function  $\phi(u)$  is different for  $u > 3/2$  and  $u < 3/2$ . For  $u > 3/2$

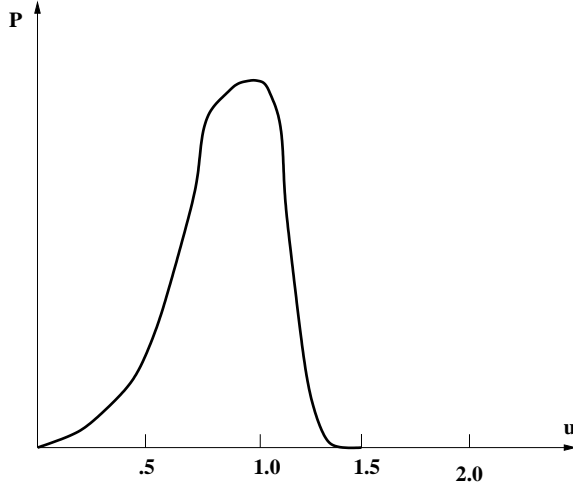


Figure 3: Asymptotic distribution function as a function of droplet's radius  $u$

the distribution function  $\phi(u)$  is determined by the evolution of the distribution at previous times and for even larger  $u$ . Since the function decays very quickly with increasing  $u$ ,  $\phi(u) = 0$  if  $u > 3/2$  and  $\tau \rightarrow \infty$ . If  $u < 3/2$  and  $\tau \rightarrow \infty$  the universal distribution develops. In the limit of large times  $\tau$ , when almost the whole excess  $Q$  is condensed into droplets, the constraint of matter conservation looks as follows:

$$\kappa e^\tau \int_0^u u^3 \phi(u, \tau) du = 1; \quad \kappa = \frac{4\pi a_c(0)^3 c_w}{3Q c_\infty}. \quad (29)$$

Since the right-hand side of Eq (29) does not depend on  $\tau$ , its left hand side should not depend on it either. So,

$$\chi[\tau - \tau(u)] = A e^{-\tau + \tau(u)} = A e^\tau P(u). \quad (30)$$

Substituting Eq (30) into the integral for  $\tau(u)$  in Eq (29), we obtain  $P(u) = \exp[\tau(u)]$ :

$$P(u) = \begin{cases} \frac{3^4 e}{2^{5/3}} \frac{u^2}{(u+3)^{7/3} (3/2-u)^{11/3}} \exp\left[-\frac{3}{3-2u}\right], & u < \frac{3}{2}; \\ 0, & u > 3/2. \end{cases} \quad (31)$$

The function  $P(u)$  (shown in Fig 3) is automatically normalized

$$\int_0^{3/2} du P(u) = 1.$$

The constant  $A$  is calculated numerically, which gives  $A = .9/\kappa$ . So, the total number of droplets  $N$  in the unit volume is:

$$N = \int da f(a, t) = \int du \phi(u, \tau) = A e^{-\tau} = \frac{2.05}{t}. \quad (32)$$

Also, we have

$$\int du P(u)(u-1) = \int e^{\tau(u)}(u-1) \frac{du}{-u} = 0. \quad (33)$$

The last equality in (33) can be obtained if  $u-1$  is found from Eq (20). Therefore, the mean dimensionless radius  $\bar{u}$  of a droplet is

$$\bar{u} = \int u du P(u) = \int du P(u) = 1, \quad (34)$$

i.e. it is equal to the critical radius  $a_c(t)$  at over-saturation, characteristic for a given time  $t$ . Finally, the radius of a droplet and the current critical radius at a given time  $t$  is

$$\bar{a} = \left( \frac{4\sigma D c_\infty}{9c_w} t \right)^{1/3}.$$