Lecture 20

Review: Nucleation, Phenomena, activated creation of drops.

\[ \Gamma(R) \]

\[ \text{chem.} \quad \delta \mu = \mu - \mu_e = \frac{1}{\rho_1 \rho_2} \frac{2 \sigma}{R} \quad \text{G.T.} \quad \text{B.C.} \]


\[ \frac{\rho_0}{\rho_1} \quad \frac{\rho_0}{\rho_2} \]

Free energy of formation:

\[ \Delta \Gamma = \frac{4 \pi}{3} R^3 \left( \rho_0 - \rho_1 \right) \left[ \mu_e - \mu_0 \rho_0 \right] + \frac{4 \pi \sigma R^2}{\delta \mu} \]
There is also a surface contribution associated with the free energy cost of the surface of the drop:

$$\Delta F_s(R) = 4\pi R^2 \sigma$$

Thus

$$\Delta F(R) = -\frac{4}{3} \pi R^3 (\rho - \rho_0) \delta \mu_0 + 4\pi R^2 \sigma$$

\[
\begin{array}{c}
\Delta F \\
\Delta F^* \\
R^* \\
R
\end{array}
\]

"free energy formation"

The maximum occurs when \( \frac{d}{dR} \Delta F = 0 \)

or

$$\delta \mu_0 (\rho - \rho_0) = \frac{2 \sigma}{R^*} = \delta \mu (\rho_1 - \rho_2)$$

But this is a \underline{G-T} condition back! This is as it should be since the \underline{G-T} relation was derived assuming \underline{stationary conditions}. The drop with \( R = R^* \) is \underline{stationary} in the sense that in the absence of stochastic thermal forces:
drops with \( R < R^* \) will shrink

drops with \( R > R^* \) will grow

and ultimately become the \( \beta \) phase.

We can also now see that \( \Delta \mu_0 \approx \Delta \mu \)

which is the "supersaturation" available
to drive the phase transition. Since,

\[
R^* = \frac{2\sigma}{\Delta \mu \Delta \rho}
\]

the critical nucleus is largest for very small supersaturations or quench depths.

The nucleation barrier is:

\[
\Delta F(R^*) = \Delta F^* = \frac{16\pi}{3} \sigma^3 (\Delta \mu \Delta \rho)^{-2}
\]

Since the nucleation rate goes as

\[
\text{rate} = \nu e^{\frac{-\Delta F^*}{k_B T}}
\]

the rate is extremely sensitive to the degree of supersaturation \( \Delta \mu \). Once

\( \Delta \mu \) is large enough that \( \Delta F^* \approx k_B T \),
nucleation will occur very rapidly. However,
we expect that the whole Kramer's-like
approach breaks down when \( \beta \Delta F^* \approx 1 \).
E. Growth and the Lifshitz-Slyosov Theory

Let's now examine the growth kinetics of a single drop that has exceeded the critical size, \( R > R^* \). The drop will grow by the slow diffusion of molecules to join the cluster. We have

\[ m_2 = m_e + \Delta m \]

Under quasi-static conditions, we need to solve

\[ \frac{d^2 \mu}{dr^2} + \frac{2}{r} \frac{d \mu}{dr} + \mu (r) = 0 \]

Subject to

\[ \mu = \mu_0 + \frac{2\sigma}{\Delta P R(t)} \text{ at } r = R(t) \]

\[ \mu = \mu_0 \quad r \to \infty \]

\[ \mu \text{ finite} \quad r \to 0 \]

The solution is:

\[ \mu(r) = \mu_0 - \frac{R(t)}{r} (\Delta \mu_0 - \frac{2\sigma}{\Delta P R(t)}) \quad r > R(t) \]

\[ = \mu_0 + \frac{2\sigma}{\Delta P R(t)} \quad r < R(t) \]

\[ \Delta \left[ \frac{2\mu}{R(t)} \right] = \left. \frac{1}{R(t)} \left[ - \frac{R(t)}{r} (\Delta \mu_0 - \frac{2\sigma}{\Delta P R(t)}) \right] \right| \quad r = R(t) + \]

\[ = \frac{1}{R(t)} (\Delta \mu_0 - \frac{2\sigma}{\Delta P R(t)}) \]
Hence, the interfacial velocity is

\[
\frac{d}{dt} R(t) = \nu = -\frac{\Delta}{(-\Delta \rho)} \Delta \left(\frac{\partial}{\partial n}\right)
\]

\[
= \frac{\Delta}{\Delta \rho} \frac{1}{R(t)} \left( \Delta \rho_0 - \frac{2 \sigma}{\Delta \rho R(t)} \right)
\]

write

Let's define:

\[
\Delta \rho_0 = \rho_0 - \rho_c = f''(\rho_c)(\rho_0 - \rho_c)
\]

\[
D \equiv \Delta f''(\rho_c) \quad "\text{diffusivity}"\]

\[
\Delta \equiv \frac{\rho_0 - \rho_c}{\rho_1 - \rho_c} \quad "\text{dimensionless supersaturation}"\]

\[
d_0 \equiv \frac{\sigma}{f''(\rho_c)(\rho_0 - \rho_c)^2} \quad "\text{capillary length}"\]

\[
\text{so}\quad \frac{d}{dt} R(t) = \frac{D}{R(t)} \left( \Delta - \frac{2 d_0}{R(t)} \right)
\]

Notice that \( \frac{dR}{dt} \to 0 \) for \( R = R^* = \frac{2 d_0}{\Delta} \)

which is another equivalent form for the critical drop size. This form predicts

for \( R \gg R^* \) or long times that

\[
R(t) \sim \sqrt{2 D \Delta t} \sim t^{1/2}
\]
The $t^{1/2}$ growth formula is correct for a single nucleus. However, in a real system, there will be a large number and as they grow, their diffusion fields will interact, with the net effect that the supersaturation gets "used up":

$$\Delta = \frac{\rho_0 - \rho_0}{\rho_0 - 1} \rightarrow 0$$

A self-consistent "mean-field" theory of the long-time growth for small initial supersaturations $\Delta_0 \ll 1$, was presented in a classic paper by Lifshitz and Slyozov, 1961. We present here a simpler version due to Langer.

Consider a system prepared with small initial supersaturation $\Delta_0 \ll 1$. 

![Diagram showing the relationship between $P$ and $P_0$.]
Since $R^* \sim \frac{1}{\Delta_0}$, $\Delta F^* \sim \frac{1}{\Delta_0^2}$, the initial nucleus size is large and the nucleation rate exponentially small. Define a droplet size distribution for

$$f(R, t) \, dR = \text{density of droplets at time } t \text{ with sizes between } R \text{ and } R + dR$$

Since $A$ will decrease with time, the nucleation rate will get even smaller; hence we consider only droplet growth and not nucleation of new droplets. Since the total # of droplets is conserved,

$$\frac{\partial}{\partial t} f(R, t) = - \frac{\partial}{\partial R} \left[ j(R, t) \right]_{\text{current}}$$

We write

$$j(R, t) = v(R, t) \, f(R, t) \quad \text{"mean-field approx"}$$

where $v(R, t)$ is the growth velocity $\frac{dR(t)}{dt}$ of a droplet of size $R$ in a medium with supersat. $\Delta(t)$ at time $t$. From our previous results,
\[ u(R, t) = \frac{D}{R} \left( \Delta(t) - \frac{2d_0}{R} \right) \]

Defining a \( t \)-dependent critical droplet radius,

\[ R^*(t) = \frac{2d_0}{\Delta(t)} \quad \text{for} \quad R < R^*(t) \quad \text{drops shrink} \]

\[ R > R^*(t) \quad \text{drops grow} \]

\[ u(R, t) = \frac{2d_0 D}{R} \left[ (R^*(t))^{-1} - R^{-1} \right] \]

Next, we define the 0th and 1st moments of the droplet size distribution:

\[ N(t) = \int_{R^*(t)}^{\infty} dR \cdot f(R', t) \quad \text{# density of condensate drops} \]

\[ \bar{R}(t) = \frac{1}{N(t)} \int_{R^*(t)}^{\infty} dR \cdot R \cdot f(R', t) \]

and develop EOMs for these:
\[ \frac{d}{dt} N = \frac{d}{dt} \int_{\mathbb{R}^n} f(r, t) \, dr + \int_{\mathbb{R}^n} \frac{\partial}{\partial t} f(r, t) \, dr - \int_{\mathbb{R}^n} \frac{\partial}{\partial r} f(r, t) \, dr \]

so

\[ \frac{d}{dt} N = -\frac{d}{dt} \int_{\mathbb{R}^n} f(r, t) \, dr \]

\[ \frac{d}{dt} R(t) = -N^{-2} \frac{dN}{dt} \int_{\mathbb{R}^n} \frac{\partial}{\partial r} f(r, t) \, dr + N^{-1} \frac{d}{dt} \int_{\mathbb{R}^n} \frac{\partial}{\partial r} f(r, t) \, dr \]

\[ + N^{-1} \int_{\mathbb{R}^n} \frac{\partial}{\partial r} f(r, t) \, dr \]

\[ = -N^{-1} \frac{dN}{dt} \left( -N^{-1} \frac{d}{dt} R^* f(R^*) \right) \]

\[ -N^{-1} \left\{ -\int_{R^*} \frac{\partial}{\partial r} u f + \frac{\partial}{\partial t} f \right|_{R^*} \right\} \]

\[ \frac{d}{dt} R = N^{-1} \frac{d}{dt} f(R^*) \left[ R - R^* \right] \]

\[ + N^{-1} \int_{R^*} \frac{\partial}{\partial r} u f \]