HW4 SOLUTION

1) Charging energy of the droplet

To calculate energy of a charged droplet, we consider a uniformly charged sphere of radius R with the charge density being equal to $\delta\rho = e\delta n$. Using Gauss law ($\int_S \vec{E}d\vec{A} = \frac{Q_{enc}}{\epsilon_0}$), it is easy to show that electric field inside/outside sphere is given as

$$E(r) = \begin{cases} \frac{e\delta n}{3\epsilon_0}r & \text{for } r < R \\ \frac{e\delta n R^3}{3\epsilon_0 r^2} & \text{for } r > R \end{cases} \tag{1}$$

Then the energy of such a charged sphere can be calculated as

$$W_C = \frac{\epsilon_0}{2}\int_{allspace} E^2 d\tau = \frac{4\pi(e\delta n)^2}{15\epsilon_0}R^5 \propto cR^5, \tag{2}$$

where constant $c = \frac{4\pi(e\delta n)^2}{15\epsilon_0}$.

2) Free energy balance

It was shown in the class that for uncharged droplet free energy balance is given as:

$$\Delta F(R) = -\frac{4\pi}{3}\Delta f_{lg}R^3 + 4\pi\sigma R^2, \tag{3}$$

where the first term stands for the bulk free energy gain and the second one describes the energy cost due to surface formation.

However, when the system is charged, the free energy balance includes an additional term accounting for the charging energy of the droplet. In such a case the free energy balance reads:

$$\Delta F(R) = aR^2 - bR^3 + cR^5, \tag{4}$$

where we introduced the following constants: $a = 4\pi\sigma, b = \frac{4\pi}{3}\Delta f_{lg}$.

The plot of $\Delta F(R)$ as function of R is shown in Fig.1. For small R, surface term prevails and $\Delta F \propto R^2$; for large R the Coulomb term wins and $\Delta F(R) \propto R^5$, in between $\delta F(R)$ is mediated by R^3 term.
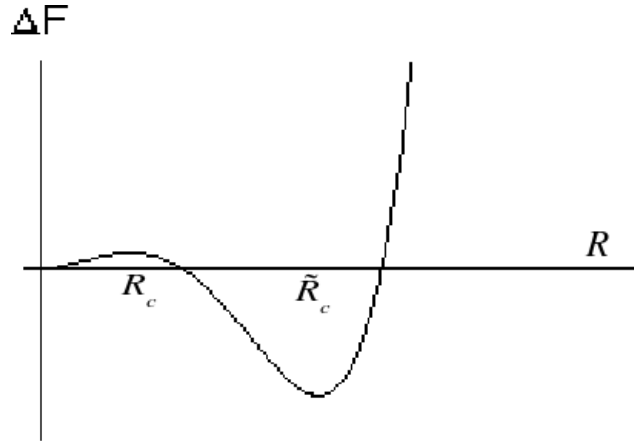

FIG. 1: Free energy as function of the droplet radius R

For a supercooled gas, we expect liquid droplets being formed as a result of density fluctuation present in the system. If a created droplet is too small $R < Rc$, the system trying to restore the equilibrium will move to the minimum free energy state, which in this case correspond to $R = 0$. In other words, created droplet will shrink and disappear. If somehow a sufficiently large droplet is created (larger then critical size $R > Rc$), it will continue to grow, lowering its free energy. However, the droplet will not get exponentially large (like in uncharged system), instead, its size will be limited to $\tilde{R}_c$. Thus, we conclude, that for charged systems droplet's size is limited by Coulomb energy, and system

instead of being globally phase separated (with exponentially large droplet occupying the bulk of the system) will achieve local phase separation in the form of the droplets with optimum size $\tilde{R}_c$. Similar Coulomb-frustrated phase separation scenario take place in high-Tc cuprates, manganites...

3) Characteristic size of Coulomb-limited droplets

To determine the characteristic size of such Coulomb-limited droplets in equilibrium, one needs to minimize the free energy $\Delta F(R)$ with respect to the droplet radius R, and solve the corresponding equation

$$\frac{\partial \Delta F(R)}{\partial R} = 0, \tag{5}$$

which in our case is in the form:

$$5c\tilde{R}_c^{\ 3} - 3b\tilde{R}_c + 2a = 0 \tag{6}$$

(trivial root $R = 0$ is neglected). In general, this equation can be solved numerically or analytically (for example, using Cardano's method). However a relatively simple analytical solution can be obtained when large dilute charged droplets (with $\delta n \to 0$) are formed in the case of a very small surface tension. For such large droplets we can ignore the surface term, and the free energy balance takes the form:

$$\Delta F(R) = -bR^3 + cR^5. \tag{7}$$

The characteristic droplet size, found as minimum of this expression is given as

$$\tilde{R}_c = \sqrt{\frac{3b}{5c}}. \tag{8}$$

4) Long-time dynamics of Coulomb-limited droplets

Based on the arguments presented above in (1)-(3), we expect the following behavior of the system. For $T < T_c$, as soon as system overcomes nucleation energy barrier determined by $E_{nc} = \Delta F(R_c)$, (in other words, as soon as $R > R_c$), droplets start to grow until they reach the optimum size $\tilde{R}_c$. Because of thermal fluctuations such Coulomb-limited droplets are not stable, and there is a finite probability that "inverse nucleation" process starts to happen. Similarly to nucleation process, in order for such "inverse nucleation" to occur, system again has to overcome energy barrier. Now we call it the "evaporation barrier" $E_{ev} = \Delta F(R_c) - \Delta F(\tilde{R}_c)$. If fluctuations within the droplets are larger then E_{ev}, system will finally find itself in the region of $R < Rc$. In order to minimize the free energy droplets will finally disappear and liquid will evaporate. The rate of such "inverse nucleation" is proportional to the probability of such process given by Boltzmann factor

$$P \propto exp\left\{-E_{ev}/T\right\}. \tag{9}$$