Homework Assignement # 4

When charged carriers are introduced in otherwise insulating hosts, their interaction with other degrees of freedom often induces a short-range effective attraction, in addition to the usual (long-range) Coulomb repulsion. If only the attraction existed, it would favor the formation of a high density liquid state at low temperatures. In systems with a fixed number (i.e. average density) of particles in a given volume, such liquid condensation would normally lead to the phenomenon of global phase separation, where a part of the volume would be occupied by a high density (liquid) state, and the remaining portion by a low density (gas) phase.

In systems of charged carriers, however, such global phase separation is prohibited by the requirement of global charge neutrality. What happens in such cases? Let us first imagine that we start with a system of neutral particles with an attractive interaction, leading to liquid condensation at a given temperature T_c. If we rapidly cool the gas below T_c, the system will be trapped in a metastable supercooled vapor phase. Thermally-induced density fluctuations then lead to the process of homogeneous nucleation, and as soon as a liquid droplet of a supercritical size is formed, it will continue to grow in order to restore equilibrium. We have already seen that the size dependence of the excess free energy of such a droplet contains a bulk term describing the free energy gain of condensation and the free energy cost due to surface tension

$$\Delta F(R) = -\frac{4\pi}{3}\Delta f_{\mathrm{lg}} R^3 + 4\pi\sigma R^2. \tag{1}$$

As we know, the competition of these two terms tends to suppress droplets of sub-critical size, while allowing larger droplets to grow without bound, until the entire system assumes a phase-separated configuration.

Now let us imagine that weak but long-range Coulomb interaction is added to these particles, so we have to account for the extra charging energy of forming a high density droplet. Generally, there will be a density difference between a liquid and a gas, such that $\delta n = n_{liq} - n_{gas} > 0$. The extra charge density within the liquid droplet is therefore $\delta\rho = e\delta n$.

(1) Consider a spherical droplet of radius R, and calculate the charging energy of such a droplet, assuming that the extra charge is uniformly distributed inside the droplet.

(2) Add this charging energy to the free energy balance for the considered droplet, and plot the expression as a function of R. How will the extra charging term affect the dynamics of supercritical droplets?

(3) Determine the characteristic size of such Coulomb-limited droplets in equilibrium by minimizing $\Delta F(R)$.

(4) What is the long-time dynamics of such Coulomb-limited droplets? Can you imagine the process of "inverse nucleation" by which such a droplet would evaporate? Can you estimate the rate for such a process, following ideas for conventional homogeneous nucleation?