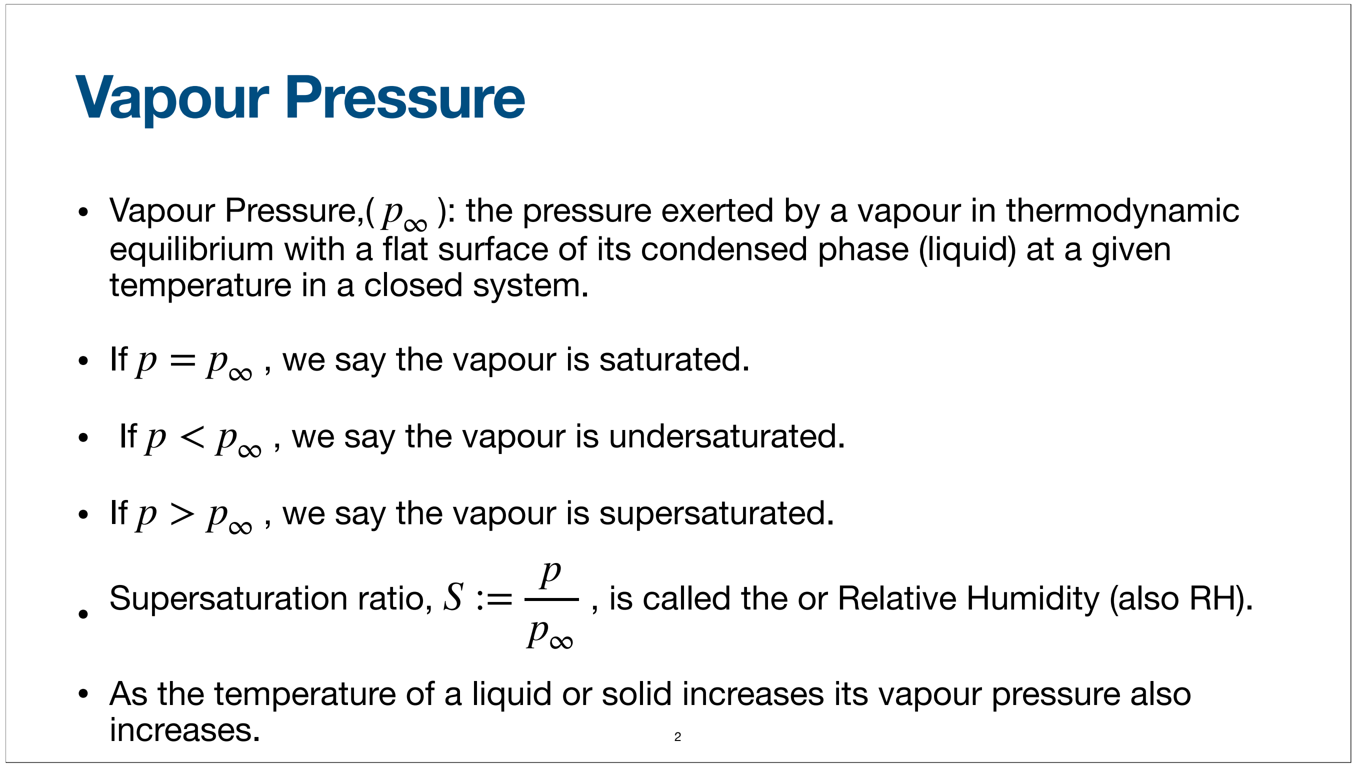
Homogeneous Nucleation

Classical Nucleation Theory

Vinay Kumar, 21st January 2022

Hi everyone. So I’ll be speaking on Homogenous nucleation. Feel free to stop and ask me to clarify any point or more likely correct me if I am wrong at any point. Lets dive in.

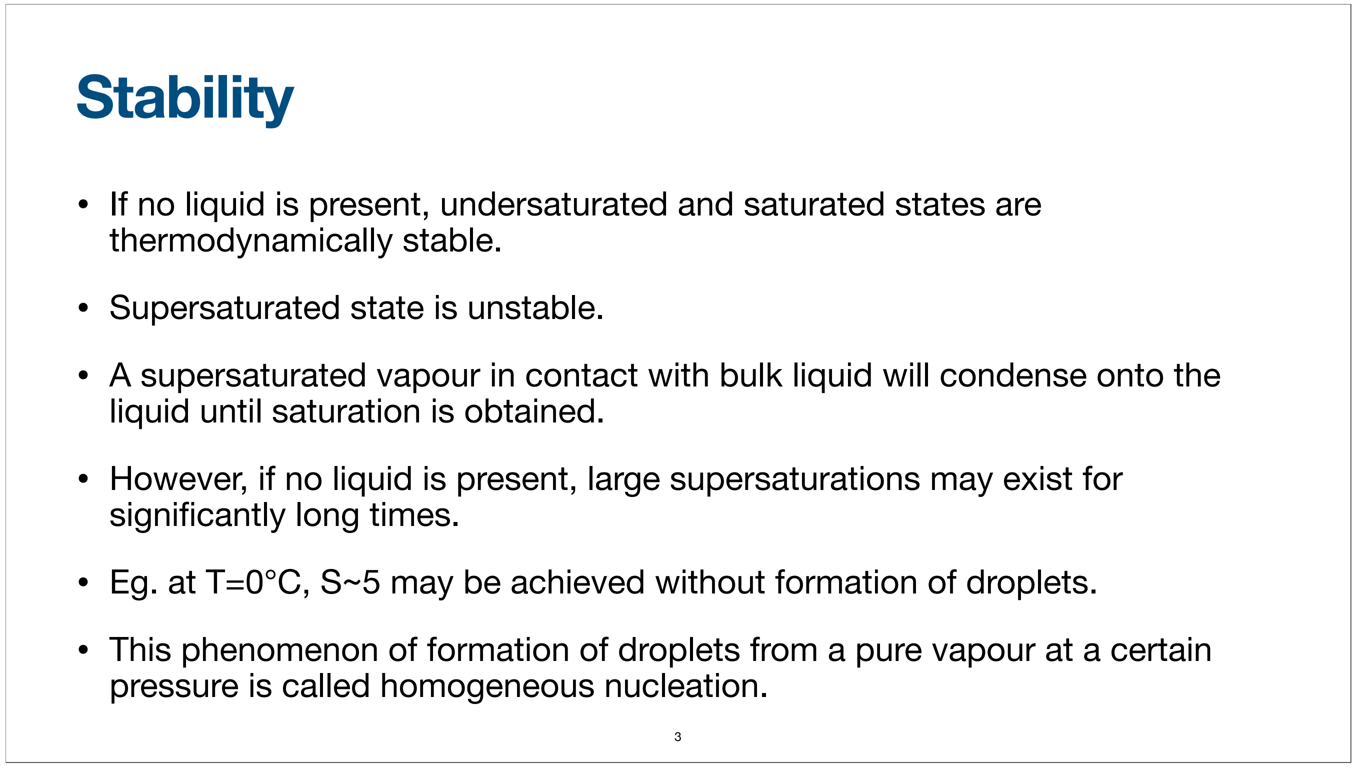


Vapour Pressure

- Vapour Pressure,(p_∞): the pressure exerted by a vapour in thermodynamic equilibrium with a flat surface of its condensed phase (liquid) at a given temperature in a closed system.
- If $p = p_\infty$, we say the vapour is saturated.
- If $p < p_\infty$, we say the vapour is undersaturated.
- If $p > p_\infty$, we say the vapour is supersaturated.
- Supersaturation ratio, $S := \dfrac{p}{p_\infty}$, is called the or Relative Humidity (also RH).
- As the temperature of a liquid or solid increases its vapour pressure also increases.

Nucleation has everything to do with vapour pressure. So I begin with defining it. Vapour pressure is defined as (read above). The infinity in the subscript denotes the radius of the flat condensed phase. If the ambient pressure is equal to the vapour pressure, …Back to slide

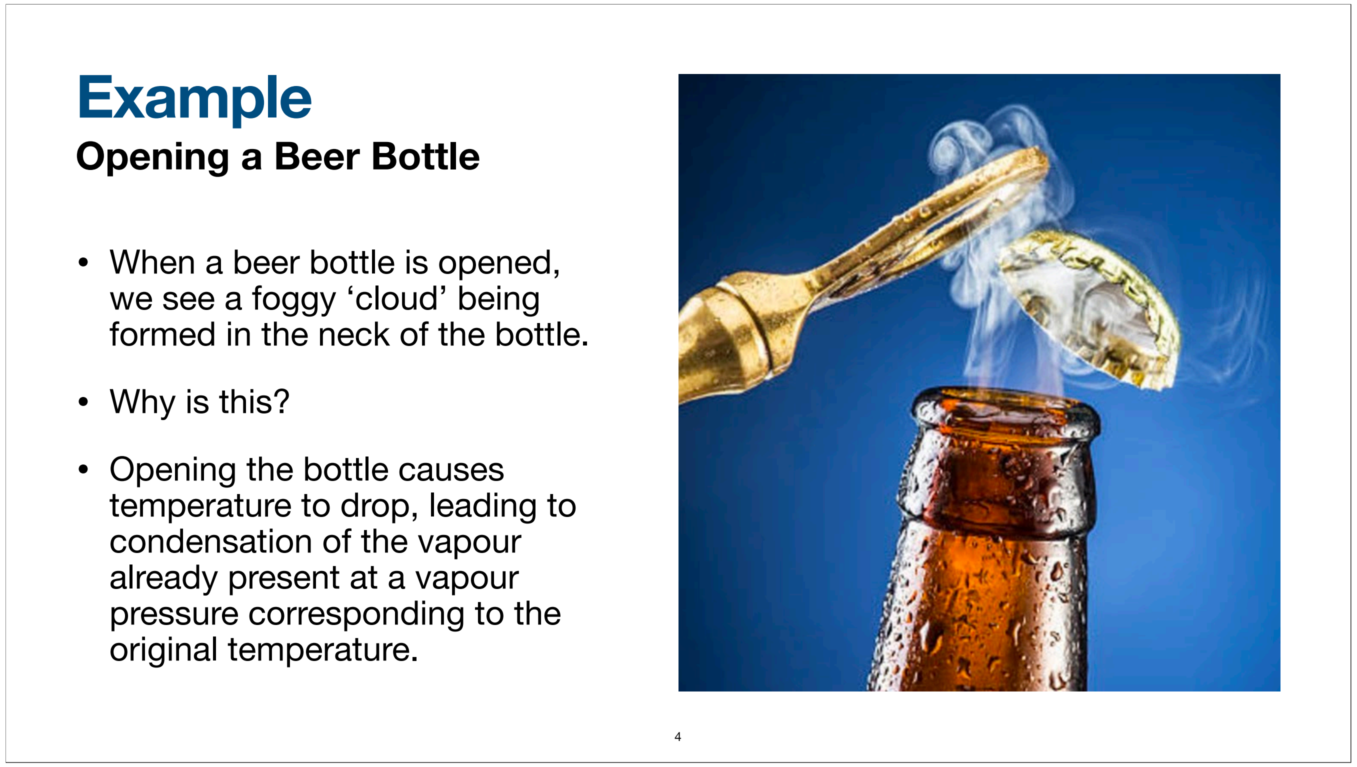
This is because: As temperature is increased, more and more of liquid particles get enough energy to escape to vapour phase. That increases the number of particles in vapour phase and hence the vapour pressure.



Stability

- If no liquid is present, undersaturated and saturated states are thermodynamically stable.
- Supersaturated state is unstable.
- A supersaturated vapour in contact with bulk liquid will condense onto the liquid until saturation is obtained.
- However, if no liquid is present, large supersaturations may exist for significantly long times.
- Eg. at T=0°C, S~5 may be achieved without formation of droplets.
- This phenomenon of formation of droplets from a pure vapour at a certain pressure is called homogeneous nucleation.

Read slide.
We'll see why a relative humidity as high as 5 does not ensure nucleation soon enough, but first let's have a look at an example of homogenous nucleation.

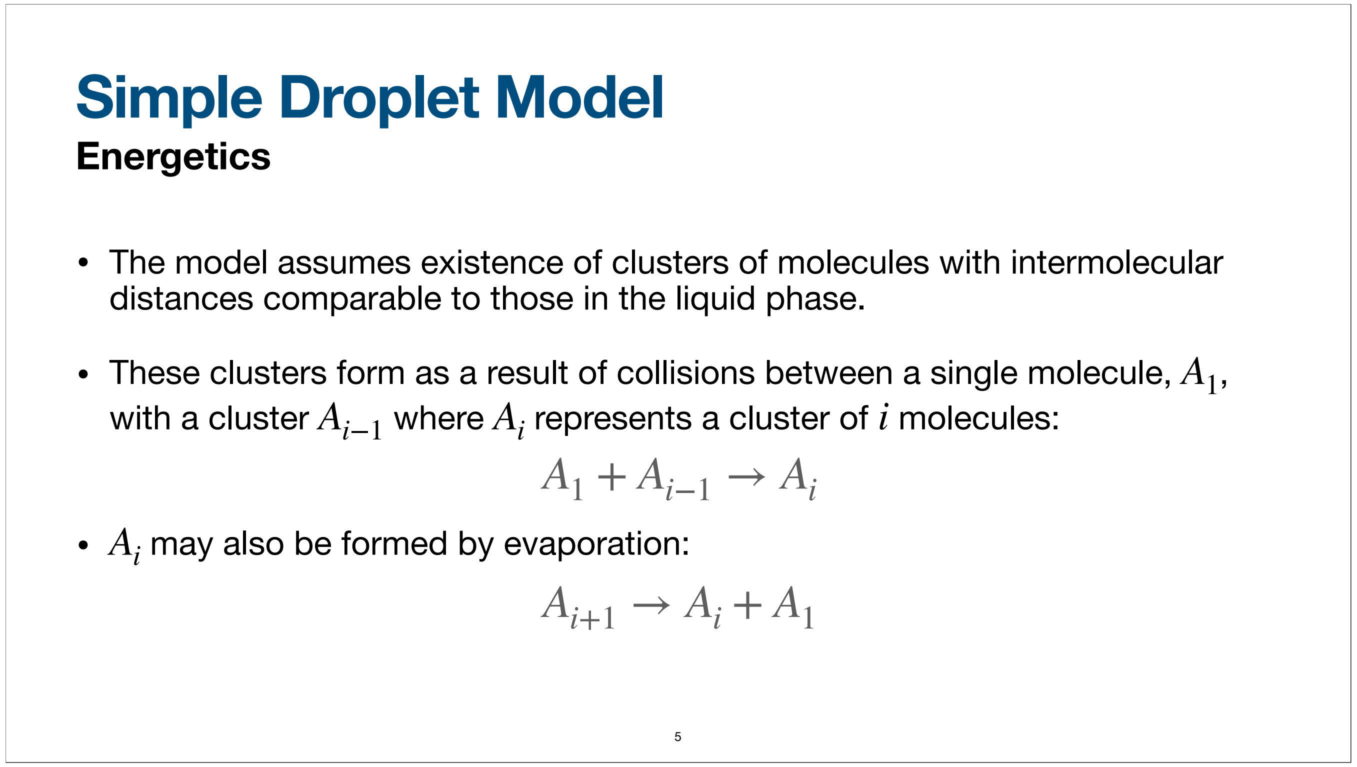


Example

Opening a Beer Bottle

- When a beer bottle is opened, we see a foggy ‘cloud’ being formed in the neck of the bottle.
- Why is this?
- Opening the bottle causes temperature to drop, leading to condensation of the vapour already present at a vapour pressure corresponding to the original temperature.

Before being opened, the water vapour above the beer bottle had had enough time in the fridge to equilibrate and attain the vapour pressure corresponding to say, 5 degree Celsius. When the bottle is opened, the temperature drop to something like negative 35 degrees Celsius. Being related to the temperature, suddenly the vapour pressure drops. The pressure of water vapour present in the neck is now sufficiently more than the vapour pressure and hence the supersaturation ratio is quite high and this causes the vapour to condense and form the cloud.



Simple Droplet Model

Energetics

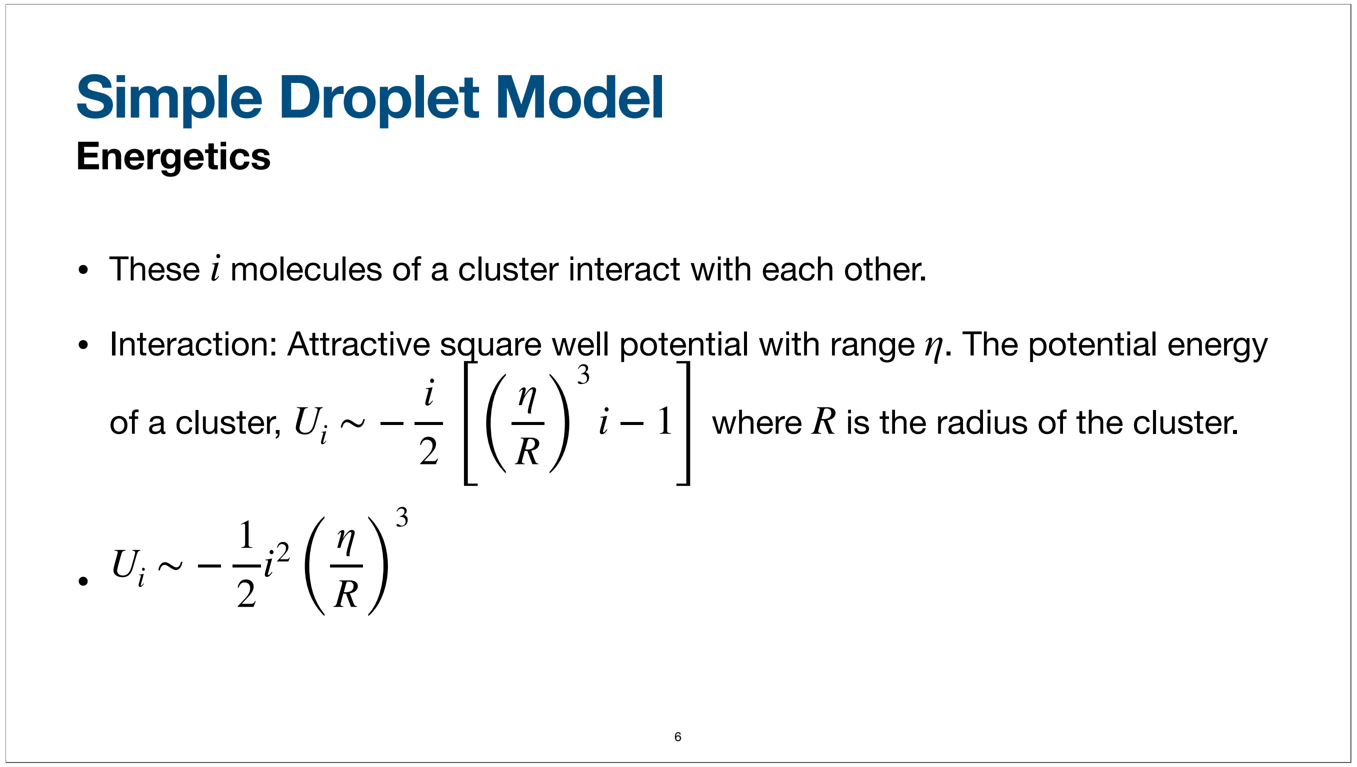
- The model assumes existence of clusters of molecules with intermolecular distances comparable to those in the liquid phase.
- These clusters form as a result of collisions between a single molecule, A_1, with a cluster A_{i-1} where A_i represents a cluster of i molecules:

$$A_1 + A_{i-1} \rightarrow A_i$$

- A_i may also be formed by evaporation:

$$A_{i+1} \rightarrow A_i + A_1$$

We work with the simplest model of nucleation where we consider how droplets form. We assume that nucleation leads to formation of clusters of molecules with small intermolecular distances, of the order of those in the liquid phase. Cluster formation takes place through either collisions between smaller clusters and molecules. Or by evaporation of a molecule from a bigger cluster.

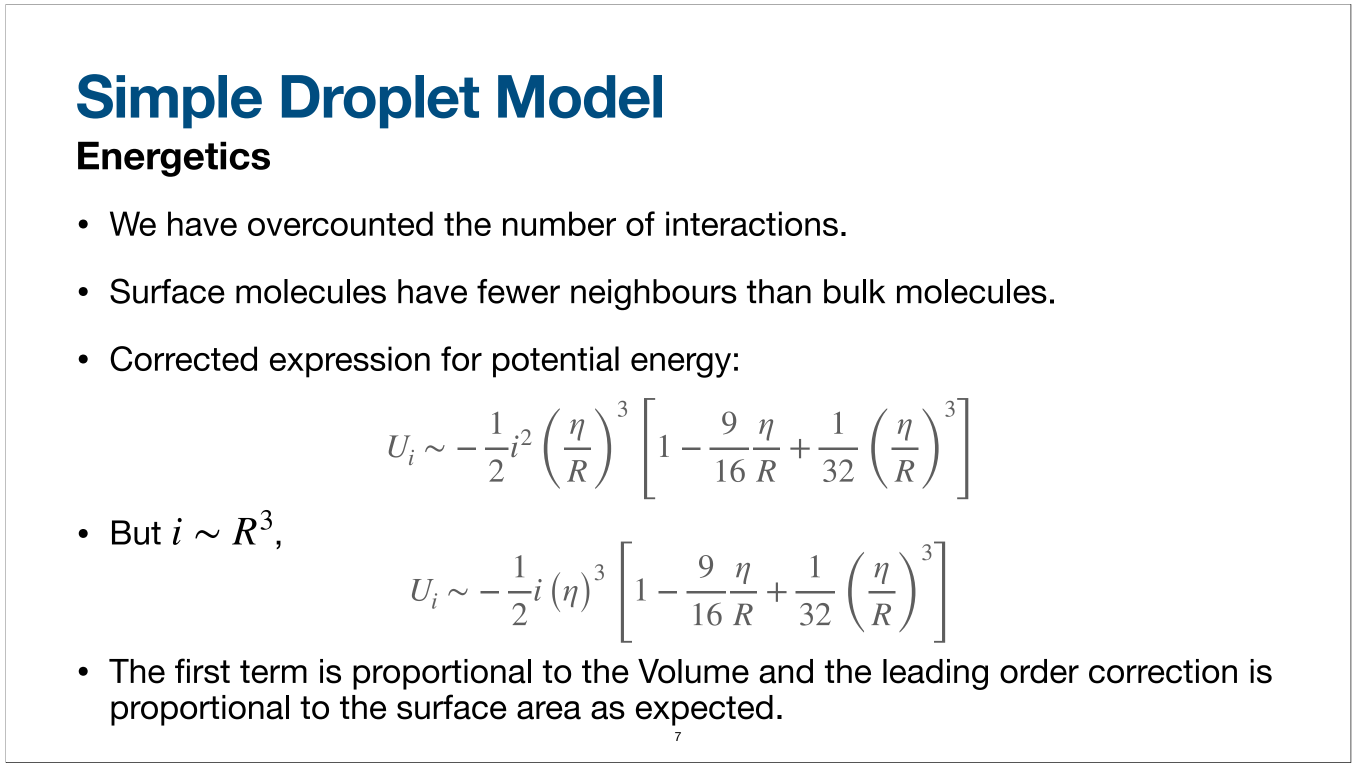


Simple Droplet Model

Energetics

- These i molecules of a cluster interact with each other.
- Interaction: Attractive square well potential with range η. The potential energy of a cluster, $U_i \sim -\frac{i}{2}\left[\left(\frac{\eta}{R}\right)^3 i - 1\right]$ where R is the radius of the cluster.
- $U_i \sim -\frac{1}{2}i^2\left(\frac{\eta}{R}\right)^3$

The molecules of the cluster interact with one another. We assume the interaction to be like an attractive square well with a range eta. The number density of molecules goes as I/(R cubed) so the number of interactions for a given molecule is (I times (eta/R-cubed) -1). And we have I molecule. So the interaction energy is I times the previous factor. But we have counted every molecule twice so we correct for that and get a 2 in the denominator. Now capital R cubed goes as I times the cube of radius of a single molecule. Which in turn is much smaller than the interaction range. So the first term in the square brackets is much larger than 1 and Ui can be approximated as below.



Simple Droplet Model

Energetics

- We have overcounted the number of interactions.
- Surface molecules have fewer neighbours than bulk molecules.
- Corrected expression for potential energy:

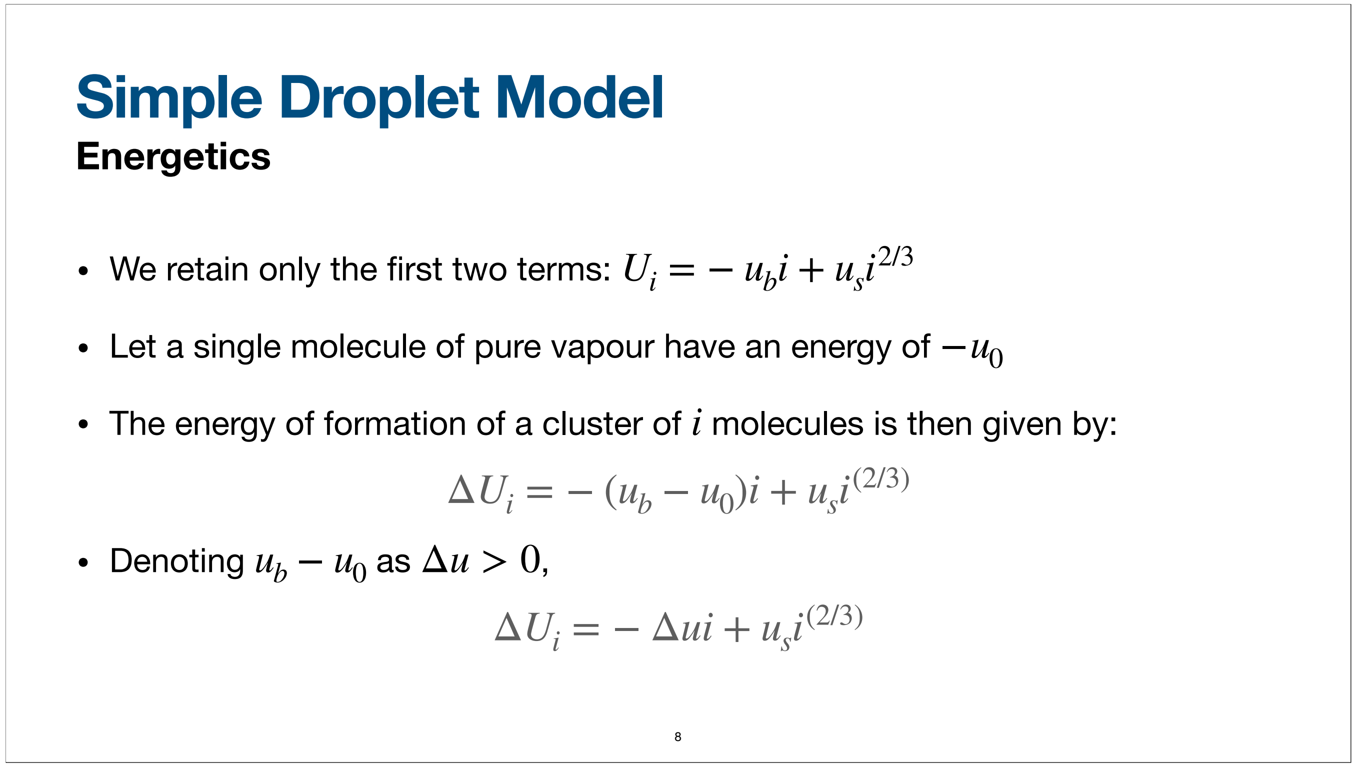
$$U_i \sim -\frac{1}{2} i^2 \left(\frac{\eta}{R}\right)^3 \left[1 - \frac{9}{16}\frac{\eta}{R} + \frac{1}{32}\left(\frac{\eta}{R}\right)^3\right]$$

- But $i \sim R^3$,

$$U_i \sim -\frac{1}{2} i \left(\eta\right)^3 \left[1 - \frac{9}{16}\frac{\eta}{R} + \frac{1}{32}\left(\frac{\eta}{R}\right)^3\right]$$

- The first term is proportional to the Volume and the leading order correction is proportional to the surface area as expected.

However, we have overcounted a bit. The molecules near the surface do not have as many neighbours to interact with as particles in the bulk do. It can be shown by simple geometric arguments that the expression for Potential energy with proper counting looks like this and replacing I with R cubed we get this. You can see that the leading order term depends on the i and hence the volume of the cluster and the leading order correction depends on I/R and hence the surface area. We'll keep terms to the second term only again remembering that eta/R^cubed term is very very small and so is its coefficient, 1/32.



Simple Droplet Model

Energetics

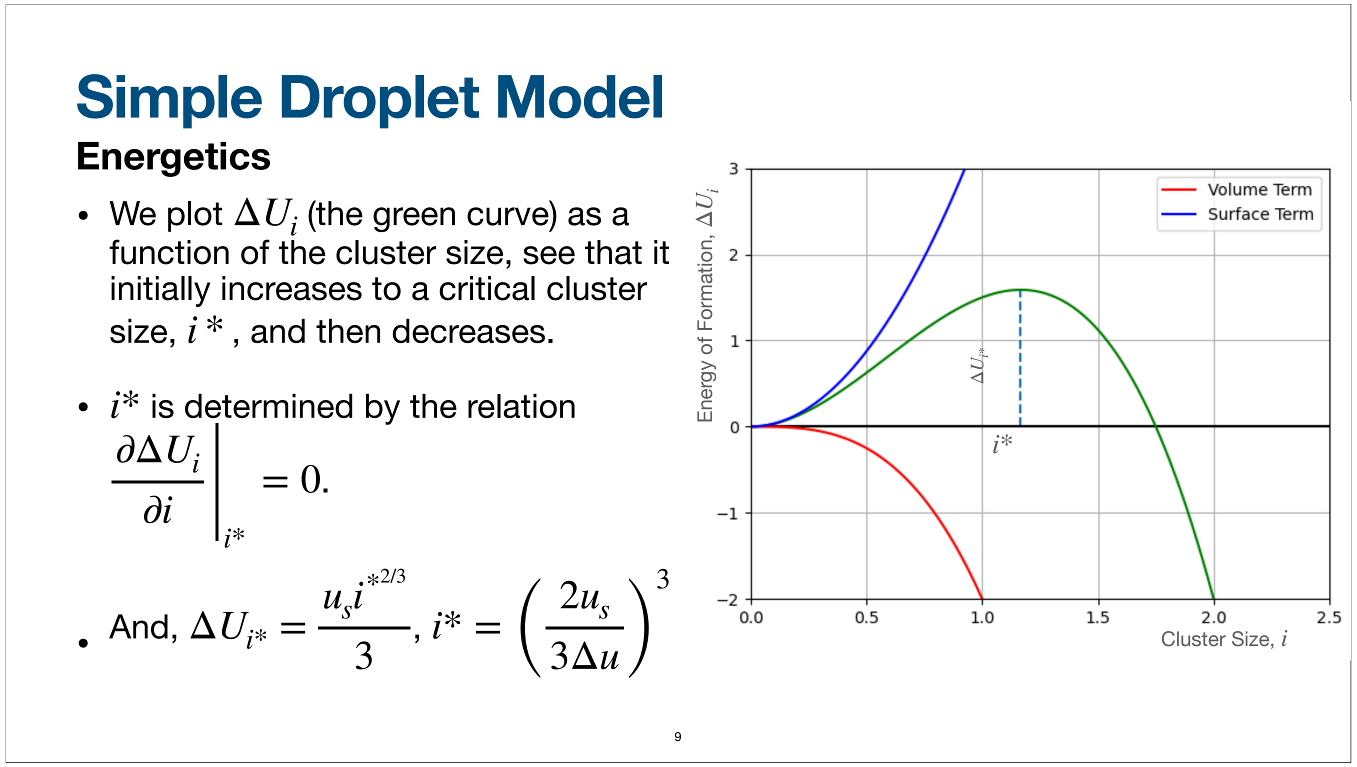
- We retain only the first two terms: $U_i = -u_b i + u_s i^{2/3}$
- Let a single molecule of pure vapour have an energy of $-u_0$
- The energy of formation of a cluster of i molecules is then given by:

$$\Delta U_i = -(u_b - u_0)i + u_s i^{(2/3)}$$

- Denoting $u_b - u_0$ as $\Delta u > 0$,

$$\Delta U_i = -\Delta u i + u_s i^{(2/3)}$$

We retain the first two terms of the expression and denote the refactors of the bulk and the surface term as u_b and u_s respectively. So minus u_b is the interaction energy between two molecules when the intermolecular distance is roughly that in the liquid phase. u_s is the surface energy of the droplet arising due to surface tension. Let the interaction energy of the molecules at distances corresponding to vapour phase be minus u_nought. Because of the attractive nature of the potential, the potential well is much deeper for liquid like intermolecular distances compared to vapour like intermolecular distances. This implies that delta small u defined as u_b minus u_nought is positive. Using this, we can get the expression for the energy of formation of a cluster of i molecules denoted by Delta capital U_i.

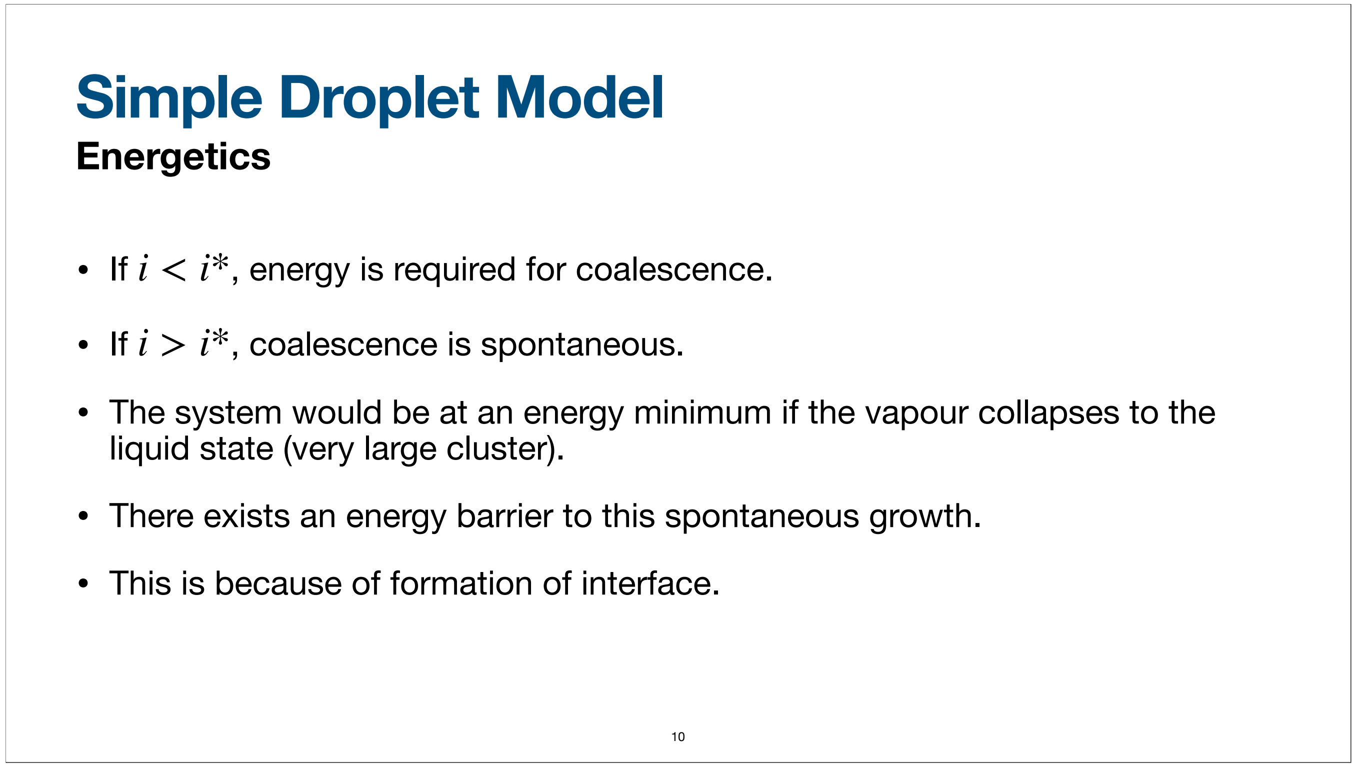


Simple Droplet Model

Energetics

- We plot ΔU_i (the green curve) as a function of the cluster size, see that it initially increases to a critical cluster size, $i*$, and then decreases.
- $i*$ is determined by the relation
  $$\left.\frac{\partial \Delta U_i}{\partial i}\right|_{i*} = 0.$$
- And, $\Delta U_{i*} = \frac{u_s i^{*2/3}}{3}$, $i* = \left(\frac{2u_s}{3\Delta u}\right)^3$

Plotting Delta U_i we get a curve shown in green. It starts increasing, attains a maximum and then drops down. The size of the cluster for which Delta U_i is maximum is called the critical size which can be determined by setting the differential of Delta U_i to zero. Note that the critical size decreases with delta small u and so does the critical energy of formation.



Simple Droplet Model

Energetics

- If $i < i*$, energy is required for coalescence.
- If $i > i*$, coalescence is spontaneous.
- The system would be at an energy minimum if the vapour collapses to the liquid state (very large cluster).
- There exists an energy barrier to this spontaneous growth.
- This is because of formation of interface.

If I have a cluster of smaller size than critical, it is clear from the previous curve that for it to grow, energy is required. For clusters bigger than the critical size, this growth is spontaneous. So for a system which started out completely as a vapour, there is an energy barrier of height Delta capital U_i star to spontaneous growth.

Simple Droplet Model

Nucleation Rate

- Assume Boltzmann distribution of clusters of various sizes: $N_i = N_1 e^{(\Delta U_i/kT)}$
- From ideal gas law, $N_1 = p/kT$
- The flux of clusters through $i*$ which is also the nucleation rate, $I \cong B_{i*} N_{i*}$
- B_{i*} = collision rate per unit area times the area = $p/(2\pi mkT)^{1/2} \times 4\pi r_0^2 {i^*}^{2/3}$

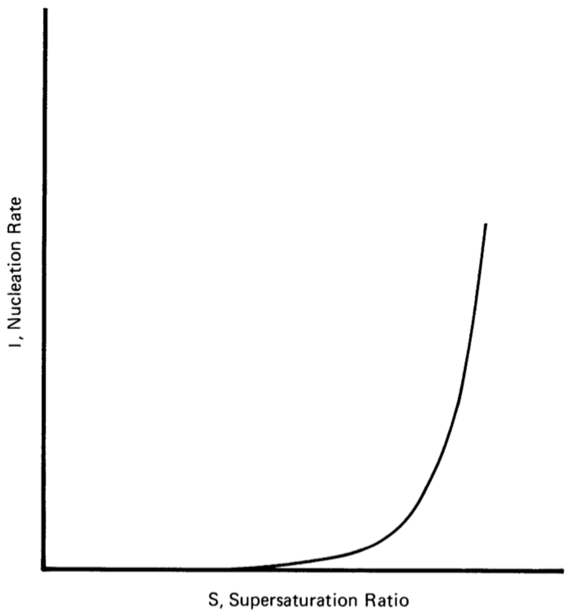
$$I = \cong [p/(2\pi mkT)^{1/2}] 4\pi r_0^2 {i^*}^{2/3} N_{i*}$$

Now we're interested in finding the rate at which the nucleation process occurs. For that, we assume that the concentration of clusters of various sizes is distributed according to the Boltzmann equation. You can see that if I put i =1, I get N1=N1 which is how we ascertain the prefactor. Obviously this expression is true for I less than I star. We also know what N1 is from the gas law. So the flux of clusters through the value I star may be approximated as B(I star) times N(I star). B(I star) is the net rate at which a cluster of critical size gains a molecule. B(I star) can be found by neglecting evaporative processes and considering only collisions. We get the rate of collisions per unit area from kinetic theory and compute B(I star) as shown. And we get an expression for the nucleation rate.

Simple Droplet Model

Nucleation Rate

- If temperature and pressure are held constant then ΔU_i is the change in the Gibbs potential.
- Also, $\Delta u = kTlnS$ and $u_s = \sigma a_0$ where S is the Relative Humidity or Supersaturation Ratio, σ is the surface tension coefficient and a_0 is the surface area per surface molecule.
- If $S \uparrow$, $\Delta u \uparrow$, $i^* \downarrow$, $\Delta U_{i^*} \downarrow$ and hence $I \uparrow$



Gibbs showed that if temperature and pressure are help constant then Delta capital U is the elevation of the Gibbs potential with respect to the vapour phase. He also showed that delta small u and u_s are given as shown. We can now see that as S increases, I star and Delta capital U decrease. And so the nucleation rate increases. The plot on the right shows the behaviour of the nucleation rate as a function of the supersaturation ratio. We see that the nucleation rate starts to rise very slowly and changes almost discontinuously. This is called the fog limit and this is where visible nucleation occurs. And that’s how we get fog over a bottle of beer.

References

- Farid Abraham - Homogeneous Nucleation Theory: The Pretransition Theory of Vapor Condensation (Advances in theoretical chemistry. Supplement)

As a famous rabbit once said, That’s all Folks. Thank you.