Aggregation During a Thermal Quench

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Motivation

Nucleation can be triggered by a change in temperature:

- Rain precipitates out of cooling humid air
- Granite crystals form as molten rock cools
- Flue gases cooled on water pipes
- Deposition in microchip fabrication (?)

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Case studies

- Aggregation with conserved monomer
- Inhomogeneous nucleation in a quenched flow
- Homogeneous nucleation in a quenched flow
- Nucleation in a thermal quench

Heuristics

- The bulk of clusters are created as two conflicting effects balance each other:
  a. Growth of clusters (decreases super-saturation)
  b. Decrease in temperature (increases super-saturation)
- Most clusters nucleate during a short “creation” era
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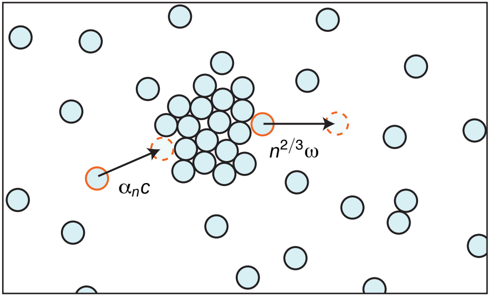
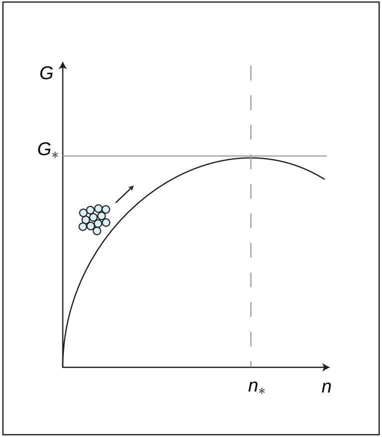
Goal: To find...

- Time-lag to creation
- Duration of creation
- Total density of cluster created
- Cluster-size distribution after creation

Becker-Döring and Zeldovich





Becker-Döring equations are obtained via detailed balance

Nucleation is due to fluctuations over a free-energy barrier

Simplifying assumptions

- The condensible vapor is dilute
- Clusters are small and grow according to Becker-Döring
- New clusters nucleate at the Zeldovich rate
- Total monomer density is conserved
- Equilibrium density is determined by Clausius-Clapeyron
- Temperature is spatially homogeneous, and slowly decreasing

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Difficulties

- Resulting PDE is non-linear, non-local
- Nucleation rate is very sensitive to super-saturation
- Duration is short relative to time-lag
- Exponentially strong dependence on cooling rate

Nomenclature and initial units

Time:	t	$\frac{1}{\omega}$
Molecular "escape" rate:	ω	
Monomer concentration:	c	c_0
Initial monomer concentration:	c_0	
Equilibrium concentration:	c_e	c_0
Cluster-size distribution:	$r(n,t)$	c_0
Super-saturation:	η	$k_B T_0$
Change in super-saturation:	$\delta\eta$	$k_B T_0$
Surface free-energy constant of a cluster:	σ	$k_B T_0$
Temperature:	T	T_0
Temperature when $c_0 = c_e$:	T_0	

Governing equations

Conservation of monomer: $c + \int_0^\infty n\, r(n,t)\, dn = 1$

Aggregation latent heat: $\varepsilon = \frac{k_B T_0}{\Lambda}$

Equilibrium concentration: $c_e = T e^{\frac{1}{\varepsilon} - \frac{1}{\varepsilon T}}$

Super-saturation: $\eta = T \log \frac{c}{c_e}$

Nucleation rate: $j = c_e \sqrt{\frac{\sigma}{6\pi}} e^{-\frac{1}{T}\frac{\sigma^3}{2\eta^2}}$

Under-cooling: $\tau = \frac{1-T}{\varepsilon} = \Omega(t + t_0)$

Growth rate: $\dot{n} = \eta n^{\frac{2}{3}}$

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A first step towards reduced equations

- For $\varepsilon \ll 1$ we have $c_e \approx e^{-\tau}$
- For $\eta \ll 1$ we have $\eta \approx \tau + \log c$
- Since the nucleation rate is highly sensitive to changes in η, we use the *change* in super-saturation, $\delta\eta = \eta - \Omega t_0$
- The super-saturation η follows τ until enough clusters take up monomer:

$$\boxed{\delta\eta - \Omega t + \int_0^\infty n\, r(n,t)\, dn = 0}$$

Finding the scales

The variables are scaled using dominant balances in the equations:

Growth: $\frac{1}{[t]} = \Omega t_0 [n]^{-\frac{1}{3}}$

Nucleation rate: $\Omega t_0 [n]^{\frac{2}{3}} [r] = \sqrt{\frac{\sigma}{6\pi}} e^{-\frac{\sigma^3}{2(\Omega t_0)^2} - \Omega t_0} \equiv E$

Conservation: $\delta\eta = \Omega [t] = [n]^2 [r]$

Creation era: $[\delta\eta] = \left(\frac{\Omega t_0}{\sigma}\right)^3$

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Solving these equations gives

$$[n] = \left(\frac{\Omega^3 t_0^4}{\sigma^3}\right)^3 \quad [t] = \frac{\Omega^2 t_0^3}{\sigma^3} \quad [r] = \left(\frac{\sigma^5}{\Omega^5 t_0^7}\right)^3$$

And determine that $\frac{\Omega^8 t_0^{12} E}{\sigma^9} = 1$

The reduced equations are still non-linear

Cluster Growth PDE:	$\partial_t r + \partial_n(n^{\frac{2}{3}} r) = 0$
Nucleation Rate BC:	$n^{\frac{2}{3}} r \longrightarrow e^{\delta\eta}$ as $n \longrightarrow 0$
Conservation/Quench:	$\delta\eta - t + \int_0^\infty nr\, dr = 0$
Initial Conditions:	$r(n, 0) \equiv 0$

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PDE has characteristics $3n^{\frac{1}{3}} = t - c$ along which the flux of clusters $n^{\frac{2}{3}} r$ is constant.

Therefore, we can write $r(n, t)$ as a function of $\delta\eta$

$$r(n,t) = n^{-\frac{2}{3}} e^{\delta\eta(t - 3n^{\frac{1}{3}})}$$

Deriving an ODE for δη

With the use of the characteristics, the PDE is converted to an integral equation:

$$\boxed{\delta\eta - t + \int_0^t \left(\frac{t-t'}{3}\right)^3 e^{\delta\eta(t')}\, dt' = 0}$$

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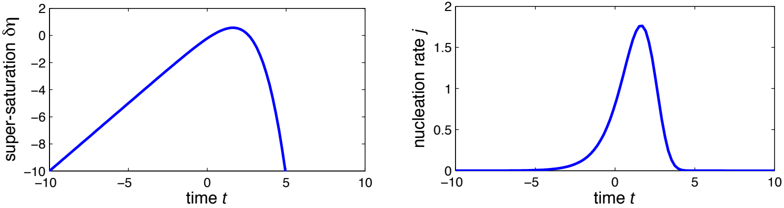
ODE for $\delta\eta$

$$\overset{....}{\delta\eta} = -\frac{2}{9}e^{\delta\eta}$$

$$\delta\eta(t_i) = t_i \quad \dot{\delta\eta}(t_i) = 1 \quad \ddot{\delta\eta}(t_i) = 0 \quad \dddot{\delta\eta}(t_i) = 0$$

The super-saturation and nucleation rate during the creation era of a quench



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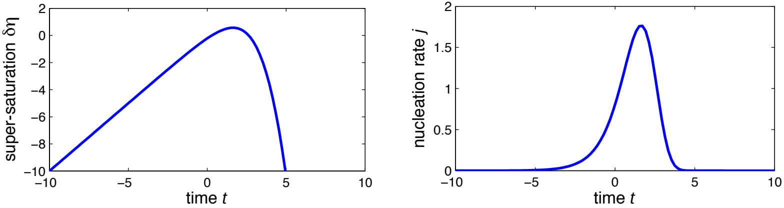

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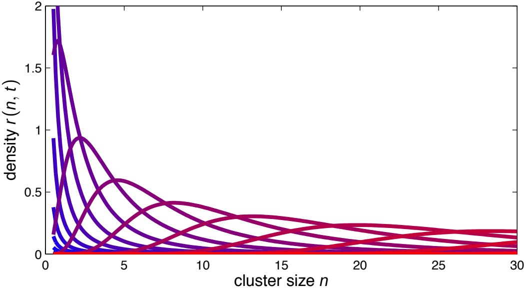

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Thank-you for your attention!