Summary. The nucleation and growth of clusters in a progressively cooled vapor is studied. The chemical-potential of the vapor increases, resulting in a rapidly increasing nucleation rate. The growth of the newly created clusters depletes monomers, and counters the increase in chemical-potential. Eventually, the chemical potential reaches a maximum and begins to decrease. Shortly thereafter the nucleation of new clusters effectively ceases. Assuming a slow quench rate, asymptotic methods are used to convert the non-linear advection equation of the cluster-size distribution into a fourth-order differential equation, which is solved numerically. The distribution of cluster-sizes that emerges from this creation era of the quench process, and the total amount of clusters generated are found.

1.1 Introduction

While studying a simplified model of nucleation the temperature is often assumed to be held constant (see, e.g., the review papers by Wu [6] and Oxtoby [5]). However, time dependence of the temperature can play an important role in the aggregation process. In this paper we study the effect that a thermal quench has on aggregation. Together with J. Neu, we previously studied [3] a similar problem with constant temperature. For a less terse literature summary, the reader is referred to the review articles cited above.

Our system comprises a dilute, condensable vapor in a carrier gas. Starting from a temperature corresponding to zero chemical-potential, the system is cooled uniformly at a constant rate. We assume a quench rate that is slow relative to the molecular timescale. This implies that the maximal chemical-potential is small and therefore the nucleation rate and cluster growth can be assumed to follow the Zeldovich formula [7] and the Becker-Döring (BD) equations [1] respectively. We use the BD equations and not diffusion limited growth, as per Lifshitz-Slyozov [4], since the final size of the clusters is relatively small. To find the value of the chemical-potential we use conservation of particles and the Clasius-Clapyron relation together with the ideal-gas
law. To simplify the model and calculation, we assume that the latent heat of evaporation is large relative to the thermal energy, \( k_B T \).

Initially, there are very few clusters and so the chemical-potential increases as the temperature drops (through the resulting reduction of the equilibrium monomer density). As the chemical-potential increases, so does the nucleation rate. Eventually, enough clusters have been created that their growth causes a large enough combined drain on the monomer density so that the increase in chemical-potential is stopped. After this, the nucleation rate drops quickly and approaches zero.

The paper is organized as follows: In Section 1.2 we present a short derivation of the aggregation model we use. In Section 1.3 we solve the resulting non-linear advection PDE using an asymptotic approximation, the method of characteristics, and a numerical solver.

### 1.1.1 Assumptions

Throughout the paper we make the following assumptions.

1. Nucleation occurs at the Zeldovich rate.
2. The clusters that form are small, and grow according to BD dynamics.
3. The process is spatially uniform.
4. The only interaction between clusters is via the chemical-potential.
5. The temperature is not affected from the condensation of clusters.
6. The carrier gas and the condensable gas are ideal gasses.

### 1.2 The Model

We briefly derive the constituent equations of the quenching process. We assume basic familiarity with standard nucleation, BD growth, and the monomer conservation argument that leads to the determination of the chemical-potential from the distribution of cluster sizes. For these we follow the notation in Wu’s review article [6]. First, we derive the relationship between the chemical-potential and the undercooling.

#### 1.2.1 Chemical-potential and the Undercooling

The chemical-potential \( \eta \) is the free energy of a monomer in condensed liquid relative to that in vapor:

\[
\eta = k_B T \log \frac{c}{c_e}. \tag{1.1}
\]

Here, \( k_B \) is the Bolzmann constant, \( T \) is the temperature, \( c \) is the ambient monomer concentration, and \( c_e \) is the equilibrium monomer concentration.

The dependence of \( c_e \) on the temperature can be found through the Clausius-Clyperon relation and the ideal-gas law as in [2].
where $\Lambda$ is the latent-energy of condensation (per monomer.) In (1.2), $T_0$ and $c_0$ are the initial equilibrium temperature and monomer-concentration. That is, at concentration $c_0$ and temperature $T_0$ the vapor phase is in equilibrium with the liquid phase. Thus, setting $T = T_0$ gives $c_e = c_0$.

We assume that $\Lambda \gg k_B T_0$ and define $\varepsilon \equiv \frac{\Lambda}{k_B T_0}$. The non-dimensional versions of $c$, $T$, and $\eta$ are:

$$\tilde{c} = \frac{c}{c_0}, \quad \tilde{T} = \frac{T}{T_0}, \quad \tilde{\eta} = \frac{\eta}{k_B T_0}. \quad (1.3)$$

Equations (1.1) and (1.2) now are as follows

$$\tilde{\eta} = \tilde{T} \log \frac{\tilde{c}}{\tilde{c}_e}, \quad \tilde{c}_e = \frac{1}{\tilde{T}} e^{\frac{1}{\tilde{T}} - \frac{1}{\varepsilon}}. \quad (1.4)$$

The undercooling is defined as $\tau \equiv \frac{1 - \tilde{T}}{\varepsilon}$.

Using the above definition of $\tau$ we find an asymptotic approximation of $\tilde{c}_e$ for small $\varepsilon$:

$$\tilde{c}_e = e^{-\tau} + O(\varepsilon \tau), \quad (1.5)$$

and the leading order approximation of $\tilde{\eta}$:

$$\tilde{\eta} \approx \log \tilde{c} + \tau, \quad \text{for } \varepsilon \ll 1. \quad (1.6)$$

### 1.2.2 The Zeldovich nucleation rate and the growth rate of clusters

Two important components of our model are the rate at which new clusters come into existence, and the rate at which existing clusters grow. The BD equations of growth specify that the size $n$ of a cluster follows the growth “law” for clusters much larger than the critical size:

$$\dot{n} = \omega \tilde{n}^{\frac{2}{3}}. \quad (1.7)$$

Where $\eta$ is as in (1.1), and $\omega$ is a “escape rate” constant so that $\omega n^{2/3}$ is the rate at which monomers leave the cluster.

The Zeldovich formula gives the nucleation rate of new clusters:

$$j = \omega c_0 \tilde{c}_e \sqrt{\frac{\sigma}{6\pi}} e^{-\frac{\tilde{c}_e^3}{2\tilde{T}^2 \tilde{\eta}}} \quad (1.8)$$

Where $\sigma$ is the “surface energy” constant of a cluster,

$$\text{surface energy} \quad \frac{k_B T_0}{\sqrt{6\pi}} = \frac{3}{2} \sigma n^{\frac{2}{3}}. \quad (1.9)$$

Using the definition of $\tau$ and (1.8) we have

$$j = \omega c_0 \sqrt{\frac{\sigma}{6\pi}} e^{-\frac{1}{\varepsilon} - \frac{1}{2\varepsilon^2} - \tau} \quad (1.10)$$
1.2.3 Growth dynamics via advection PDE

We are interested in finding the evolution of the density of cluster sizes. Let \( r(n, t) \) be the density of clusters of size \( n \) at time \( t \) (also referred to as the “distribution of cluster-sizes”). From equation (1.7) we derive an advection PDE for the distribution of clusters in the space of their size,

\[
\partial_t r + \omega \tilde{\eta} \partial_n \left( n^{\frac{3}{2}} r \right) = 0, \quad \text{in } n > 0.
\]  

(1.11)

The flux of clusters \( \omega \tilde{\eta} n^{\frac{3}{2}} r \) asymptotes to the Zeldovich rate as \( n \to 0 \), thus

\[
\omega \tilde{\eta} n^{\frac{3}{2}} r \to j = \omega c_0 \sqrt{\frac{\sigma}{6\pi}} e^{-\frac{3\sigma^2}{2\pi t^2}} \text{ as } n \to 0.
\]  

(1.12)

1.2.4 Determination of the chemical-potential

The chemical-potential can be inferred from the distribution of cluster sizes and the initial concentration \( c_0 \).

\[
c + \int_0^\infty nr(n, t) \, dn = c_0.
\]  

(1.13)

For small values of \( \eta \) we have from (1.6) that \( c = c_0 e^{\tilde{\eta} - \tau} \). Thus

\[
e^{\tilde{\eta} - \tau} + \int_0^\infty nr(n, t) \, dn = 1, \text{ where } \tilde{r} = \frac{r}{c_0}.
\]  

(1.14)

1.3 The Mathematical Problem

We now drop all tildes and refer only to non-dimensional variables. The mathematical problem is therefore,

\[
\partial_t r + \eta \partial_n \left( n^{\frac{3}{2}} r \right) = 0,
\]  

(1.15)

\[
\eta n^{\frac{3}{2}} r \to \sqrt{\frac{\sigma}{6\pi}} e^{-\frac{3\sigma^2}{2\pi t^2}} \text{ as } n \to 0,
\]  

(1.16)

\[
e^{\eta - \tau} + \int_0^\infty nr \, dr = 1.
\]  

(1.17)

Here, time \( t \) is non-dimensionalized with the scaling unit \( 1/\omega \).

In the current paper we consider an undercooling which increases linearly with time \( t \):

\[
\tau = \Omega(t + t_0).
\]  

(1.18)

The parameter \( \Omega \) is externally specified, and \( t_0 \) is a time-lag needed so that the “interesting” behavior happens near \( t = 0 \).
1.3.1 Asymptotic Solution of the Creation Era

The equations needed to find the relevant scales of the creation era are mostly straightforward dominant balances of equation (1.15–1.17). There is one that is not: The change in chemical-potential must be such that the reduction in the nucleation rate is comparable to the nucleation rate itself. This implies that the change in chemical-potential is small (relative to $\eta$ itself) and we use $\delta\eta \equiv \eta(0) - \eta(t)$ to follow the change in the chemical potential. To save space, we omit the derivation and proceed to the resulting scales. They are

$$[\delta\eta] = \left( \frac{\Omega t_0}{\sigma} \right)^3 \quad [n] = \Omega^3 t_0^3 \left( \frac{1}{\sigma^3 E} \right)^{\frac{3}{4}} \quad [t] = \left( \frac{1}{\sigma^3 E} \right)^{\frac{1}{4}} \quad [r] = \left( \frac{\sigma E}{\Omega^2 t_0^3} \right)^{\frac{2}{3}}.$$  

While $t_0$ and $\Omega$ are connected by $\Omega^2 t_0^3 E^{\frac{1}{4}} = \sigma^{\frac{3}{2}}$. We introduced $E$, a measure of nucleation rate: $E \equiv \sqrt{\frac{\pi}{6}} e^{-\frac{\sigma^3}{2(\Omega t_0)^2}} - \Omega t_0$. Using these scales results in the following system for $r(n, t)$ and $\eta$:

$$\partial_t r + \partial_n (n^{\frac{3}{2}} r) = 0, \quad (1.19)$$

$$n^{\frac{3}{2}} r \rightarrow e^{\delta\eta} \text{ as } n \rightarrow 0, \quad (1.20)$$

$$\delta\eta(t) - t + \int_0^\infty n r \, dr = 0. \quad (1.21)$$

Since $n^{\frac{3}{2}} r$ is constant along the level curves of $3n^{\frac{3}{2}} - t$, we can write

$$r(n, t) = n^{\frac{3}{2}} e^{\delta\eta(t-3n^{\frac{3}{2}})}. \quad (1.22)$$

Substituting this into (1.21) yields an integral equation for $\delta\eta$, and using the change of variable $t' = t - 3n^{\frac{3}{2}}$ we arrive at

$$\delta\eta(t) - t + \int_{-\infty}^t \left( \frac{3}{t-t'} \right)^{\frac{3}{4}} e^{\delta\eta(t')} \, dt' = 0. \quad (1.23)$$

From here we derive a fourth-order ordinary differential equation (ODE) for $\delta\eta$, by differentiating 4 times:

$$\dddot{\delta\eta} = -\frac{2}{9} e^{\delta\eta}, \quad \text{where } \delta\eta(t) \sim t, \text{ as } t \rightarrow -\infty. \quad (1.24)$$

To solve this ODE (numerically), we start with $\delta\eta(t_i) = t_i$, $\dot{\delta\eta}(t_i) = 1$, $\ddot{\delta\eta}(t_i) = 0$, $\dddot{\delta\eta}(t_i) = 0$, and $t_i = -10$.

By integrating $e^{\delta\eta}$ we get the (scaled) density of clusters $\rho$ that were formed, $\rho \approx 5.1$. The resulting density is shown in Fig. 1.1.
Fig. 1.1. The cluster size distribution $r(n, t)$ for $t$ ranging from 0 to 9 and, inset, the nucleation rate as a function of (shifted and scaled) time.

1.4 Conclusions

Thermal quench is a standard trigger for nucleation. However, normally the quench process itself is ignored and only the outcome (i.e., a super-saturated monomer solution) is considered. In this paper we have shown that during a slow quench, enough clusters nucleate so that no more nucleate after the quench. Presumably, the clusters that have nucleated simply grow after the quench and eventually coarsen.

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