LETTER TO THE EDITOR

Scaling in the kinetics of droplet growth and coalescence: heterogeneous nucleation

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Abstract. The kinetics of droplet growth in a heterogeneous nucleation process is investigated using Monte Carlo simulations, scaling theory and the Smoluchowski equation. The exponent describing the scaling of the droplet size distribution and the growth law for the mean droplet size are calculated exactly. The simulation data are found to be consistent with the theoretical predictions in $d = 1, 2$ and 3 dimensions.

The formation of a distribution of various size droplets is the common feature of a wide variety of systems, including thin films [1, 2], breath figures [3, 4], soap bubbles [5], fly ash particles [6, 7], microemulsions [8], dew, clouds [9], rain, fog, foam and froth. Motivated by experiments on thin-film growth [2], we have recently developed a scaling theory and a simple model for describing droplet growth in homogeneously nucleated processes [2]. With homogeneous nucleation [1, 2], droplets form and grow from anywhere in the system. However, there are many systems [1, 3-9] in which droplets do not form and grow spontaneously. Instead, the formation of droplets is initiated at 'impurity' centres that act as the nuclei for the droplets.

In this letter we present a scaling description and a model for describing droplet growth with heterogeneous nucleation. We show that in contrast to homogeneous nucleation, where the size distribution consists of a power-law distribution superimposed on a monodispersed distribution at large sizes, the droplet size distribution has a monodispersed bell-shaped form. The origin of this difference and its significance as far as the scaling properties of the two systems is concerned is pointed out. The exact exponents describing the size distribution and the growth law for droplet growth with heterogeneous nucleation are determined using scaling arguments. We also apply the Smoluchowski rate equation to the problem of droplet growth. Using this approach we obtain a relation between the exponents and determine the scaling form of the reaction kernel.

In order to describe droplet growth and coalescence with heterogeneous nucleation we have developed a model where initially there are a fixed number of nucleation sites in the system. The simulations are started by placing N_0 droplets of diameter d_0 in a d-dimensional system of size L^d such that there is no overlap between the droplets. In general, droplets grow by two distinct mechanisms [1, 2]. The first process is direct absorption from the vapour and the second is droplet coalescence. In a uniform vapour

density, every droplet grows at a rate proportional to its surface area. As a generalisation of this scenario, we assume that the droplet radii grow as

$$dr/dt \propto r^{\omega} \qquad (1)$$

where ω is an arbitrary exponent. At each time step in the simulations, the radius of each of the droplets is increased according to (1) using the formula

$$r' = (r^{\xi} + \delta\xi)^{1/\xi} \qquad (2)$$

where r' is the new radius, $\xi = 1 - \omega$ and δ is a small number. As the growth of the droplets continues, the separation of various droplets decreases and—upon contact— droplets coalesce to form larger droplets. In each time step, droplets are examined for possible overlaps and overlapping droplets are coalesced with mass and centre-of-mass conservation. As a generalisation of the growth and coalescence of spherical droplets, we assume that the droplets in our model are hyperspherical with a dimensionality D. When a droplet of radius r_1 touches or overlaps a droplet of radius r_2, a new droplet is formed, centred on the centre of mass of the two original droplets, with a radius r which is given by [2]

$$r = (r_1^D + r_2^D)^{1/D}. \qquad (3)$$

If this droplet overlaps one or more other droplets, they are also coalesced and this procedure continues until no overlaps remain. Some processes such as the phase transition from an isotropic to a nematic phase in liquid crystals correspond to $D = d = 3$, whereas the growth of water droplets on surfaces (e.g. breath figures) corresponds to $D = 3$ and $d = 2$, and the formation of dew on the cobweb corresponds to $D = 3$ and $d = 1$.

Figure 1 shows the distribution of the droplets at three different times during the growth in a system with $N_0 = 20\,000$, $d_0 = 1.5$, $L = 512$, $\omega = 0$, $D = 3$ and $d = 2$. In order to test for possible scaling, the lengths have been rescaled in such a way that the system size in all three figures is equal to $8d_0S^{1/3}$, where S is the mean droplet size. It is clear from these figures that the droplet size distribution is quite self-similar if the system is scaled properly. In the very early stages of the growth, i.e. before any droplet has touched and coalesced with any other droplet, all droplets have the same size. In the later stages of the growth, due to coalescence, this sharp distribution is broadened into a bell-shaped curve, as shown in figure 2, where we have plotted the droplet size
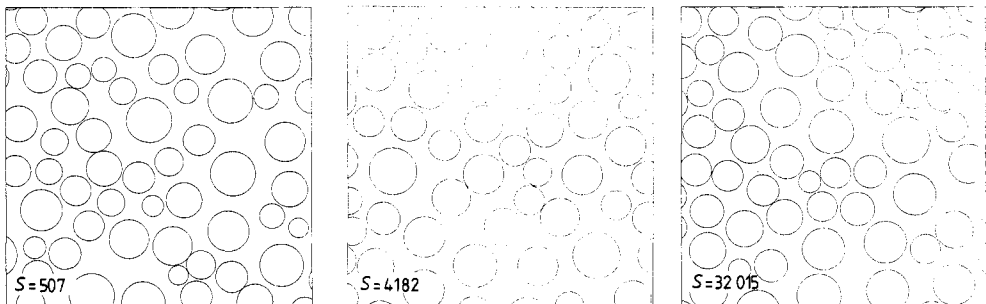

Figure 1. Sample droplet size distributions at three different times during the growth in a system with $N_0 = 20\,000$, $d_0 = 1.5$, $L = 512$, $\omega = 0$, $D = 3$ and $d = 2$. In order to show the self-similarity of the distributions we have rescaled all the lengths so that the system size is equal to $8d_0S^{1/3}$ in each case.
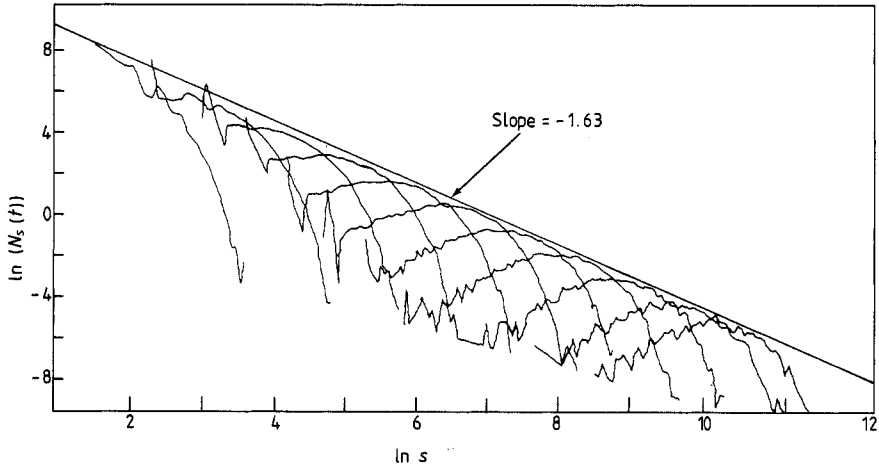
Figure 2. The droplet size distribution at different times during the growth in a system with $\omega = 0$, $D = 3$ and $d = 2$. Due to coalescence, the distribution is broadened into a bell-shaped curve. The most characteristic feature of the distribution is that the position of the peak moves to larger sizes with increasing time. At the same time the position of the peak moves down indicating that the density of large droplets decreases.

distribution at different times during the growth. The most characteristic feature of the distribution is that the position of the peak of the distribution, which is a measure of the mean droplet mass, moves to larger sizes with increasing time. On the other hand, the number density of large droplets decreases.

We can describe the process of droplet growth with heterogeneous nucleation in a way very similar to our approach for homogeneous nucleation [2]. In analogy with homogeneous nucleation [2], we assume that the number of droplets of size s at time t scales as [10, 11]

$$n_s(t) \sim s^{-\theta} f(s/S(t)) \tag{4}$$

where $S(t) = \Sigma s^2 n_s(t)/\Sigma s\, n_s(t)$ is the mean droplet size. $S(t)$ and the mean radius $R(t) \equiv S(t)^{1/D}$ diverge as

$$S(t) \sim t^z \qquad \text{and} \qquad R(t) \sim t^{z/D}. \tag{5}$$

The total number of droplets in the system, $N(t)$, which is given by $N(t) = \Sigma n_s(t)$, is expected to decrease with an exponent z' as

$$N(t) \sim t^{-z'}. \tag{6}$$

The size distribution exponent θ and the dynamic exponents z and z' may depend on ω, d and D. In addition, since the total mass in the system is not a constant, θ does not have a *superuniversal* value of 2 as in aggregation processes [10, 11]. Note that in contrast to the case of homogeneous nucleation [2], the scaling function $f(x)$ has a bell-shaped form centred around $x = 1$. Figure 3 shows how the data for various times can be scaled into a single scaling curve using (4). We have obtained equally excellent scaling plots for other values of ω and D in $d = 1, 2$ and 3.

We now show how the exponents θ, z, and z' can be determined exactly using scaling arguments. The only assumption in our calculation is that the mean droplet radius $R(t)$ is the only characteristic length in the problem. For the mass density ρ
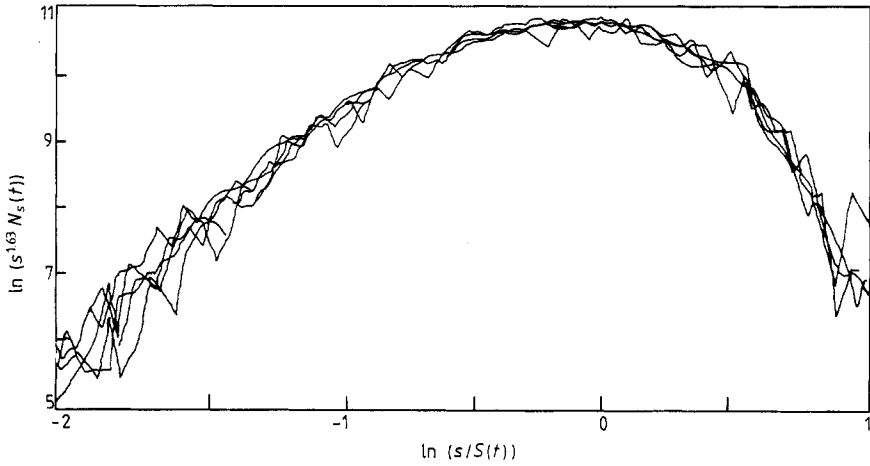
Figure 3. The data of figure 2 for various times can be scaled into a single scaling curve using (4). We have obtained equally excellent scaling plots for other values of ω and D in $d = 1, 2$ and 3 dimensions.

we can write

$$\rho \sim R^{D-d} \sim t^{z(D-d)/D}. \tag{7}$$

Using the scaling form (4) in the definition of ρ, we get

$$\rho = \Sigma s n_s(t) \sim \int ds\, s^{1-\theta} f(s/S(t)) \sim S^{2-\theta} \int dx\, x^{1-\theta} f(x)) \sim t^{z(2-\theta)}. \tag{8}$$

In comparing (7) with (8) we find

$$\theta = 1 + d/D. \tag{9}$$

This expression is the same as for large droplets in homogeneous nucleation [2] and it is independent of the rule for the growth of the individual droplets.

In order to determine the growth-law exponent z, we note that our scaling assumption indicates that the growth of the mean droplet radius is governed by (1), with or without coalescence. This implies that

$$R(t) \sim t^{1/(1-\omega)}. \tag{10}$$

Using the fact that $S(t) \sim R(t)^D$, from (5) and (10) we find

$$z = D/(1-\omega). \tag{11}$$

The exponent z' can be obtained directly from the definition of $N(t)$ and the scaling form (4). We find

$$N(t) = \Sigma n_s(t) \sim \int ds\, s^{-\theta} f(s/S(t)) \sim S^{1-\theta} \int dx\, x^{1-\theta} f(x) \sim t^{z(1-\theta)}. \tag{12}$$

In comparing (12) with (6), and substituting the values of θ and z from (9) and (11), respectively, we obtain

$$z' = d/(1-\omega). \tag{13}$$

The simulation results for various values of ω, and D in $d = 1, 2$ and 3 are in excellent agreement with predictions (9), (11) and (13).

The traditional method for studying the kinetics of aggregation processes is to use the Smoluchowski rate-equation approach [12]. Similarly, for the growth and coalescence of droplets we can write the kinetic equation

$$\frac{dn_s}{dt} = \frac{1}{2} \sum_{i+j=s} K_{ij} n_i n_j - n_s \sum_{j=1}^{\infty} K_{sj} n_j + K'_{s-1,1} n_{s-1} - K'_{s,1} n_s \tag{14}$$

where K_{ij} is the rate coefficient for coalescence of a droplet of size i with a droplet of size j and K'_{i1} is the rate of growth of droplets of size i according to (1) which is the growth rate due to absorption of monomers. The main advantage of the kinetic equation approach is that it provides a simple physical interpretation of the temporal evolution of the size distribution. The first term on the right-hand side is the rate at which droplets of size s are formed by aggregation of droplets of size i and j to form droplets of size s. The second term is the rate at which droplets of size s disappear by coalescence with droplets of size j. The third and fourth terms describe the growth of the droplets by absorption from the vapour and are manifestations of (1). The third term gives the rate at which droplets of size $s-1$ grow to form droplets of size s. The last term gives the rate at which the number of droplets of size s decreases when droplets of size s grow according to (1) to form droplets of size $s+1$.

The kinetic equation (14) provides a mean-field description of the growth and coalescence of droplets, because spatial fluctuations in the density of the droplets are neglected. Except for special cases, the kinetic equation cannot be solved for the physically interesting forms of the K_{ij}. However, using the dynamic scaling approach [10, 11], it is possible to obtain results without solving the kinetic equation directly. We assume that (14) is invariant under the transformations

$$
\begin{aligned}
s &\to bs & t &\to b^{1/z} t \\
K_{ij} &\to b^{-\lambda} K_{ib\,jb} & n_s(t) &\to b^{-\theta} n_{sb}(b^{1/z} t)
\end{aligned} \tag{15}
$$

where b is a scale factor and λ is the degree of homogeneity of the reaction kernel. Using these transformations in (14) we find the relation

$$\theta - 1/z = 1 + \lambda. \tag{16}$$

In addition, according to (1) the coefficient K'_{s1} is given by the rate of growth of the droplets, namely

$$K'_{s1} \sim ds/dt \sim s^{\nu} \qquad \text{with} \quad \nu = (\omega + D - 1)/D. \tag{17}$$

Therefore, the kinetic equation gives the same expression (11) for the growth exponent z. Substituting the exact values of θ and z from (9) and (11), respectively, in (16) we find

$$\lambda = (\omega + d - 1)/D. \tag{18}$$

If we substitute the results $1/z + \theta = 2$, and $\theta = 1 + d/D$ for homogeneous nucleation [2] in (16), we find

$$\lambda = (2d/D) - 1. \tag{19}$$

It would be instructive to obtain the reaction kernels directly in order to test relations (18) and (19).

We now compare and contrast heterogeneous droplet growth with homogeneous nucleation. The growth of large droplets in homogeneous nucleation is governed by

the rate at which a droplet absorbs small droplets from the vapour. Assuming a uniform vapour density, the rate of growth of the droplets is proportional to their area, i.e.

$$d(R^D)/dt \propto R^d. \tag{20}$$

This implies that $R \sim t^{1/(D-d)}$. In comparing this result with (10), we find that $\omega = 1 - D + d$ for the growth of large droplets in homogeneous nucleation. Substituting this value of ω into (11) we find $z = D/(D - d)$, in agreement with the results reported in [2].

The main difference between homogeneous nucleation and heterogeneous nucleation is the continuous replenishment of monomers and small droplets in the case of homogeneous nucleation. This is reflected in the appearance of two types of size distributions in the homogeneous nucleation system: a power-law decay at small sizes, indicating a polydispersed distribution, is superimposed on a bell-shaped curve at larger droplet sizes and is given by the exponents θ and z given in [2]. The bell-shaped distribution arises from the growth and coalescence of large droplets. The polydispersed part of the distribution, which does not exist in the case of heterogeneous nucleation, is due to the continuous feeding of the monomers and nucleation of small droplets. The fact that a source of particles leads to the formation of a steady-state power-law size distribution in an aggregation process has been recognised already in the case of cluster–cluster aggregation in the presence of a source and a sink [13].

In summary, the formation of a distribution of droplets is ubiquitous in nature [14], from thin films to water droplets in rain and clouds. We have shown that the scaling description is an effective method for describing the kinetics of droplet growth. We have also developed a simple model which captures the essential physics of droplet growth and can be used for further investigations of droplet growth phenomena.

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