LETTER TO THE EDITOR

Effects of Brownian coagulation on droplet growth in a quenched fluid mixture

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Abstract. We study the effect of Brownian coagulation driven by the thermal motion of droplets on the competitive droplet growth in a quenched binary fluid. To consider such an effect, we extend the classical theory of the Ostwald ripening by using a systematic method that was originally proposed by Lifshitz and Slyozov for the case of the encounter mechanism. We discuss the effect of Brownian coagulation on the asymptotic form of the droplet size distribution function and the growth law of the average droplet size.

In the present letter we study the droplet growth in a quenched binary fluid driven by two mechanisms—that is, the evaporation–condensation mechanism and the Brownian coagulation. In off-critically quenched binary systems (alloy and fluid mixture), the former mechanism results in the competitive droplet growth called Ostwald ripening [1, 2]. On the other hand, it has been pointed out [3, 4] that the Brownian coagulation, or the collision arising from thermal motion of droplets, plays an important role in a quenched binary fluid only. It has also been shown [4] that this coagulation is negligible compared with the evaporation–condensation mechanism in alloy systems.

It has been pointed out by Lifshitz and Slyozov (LS) [1] that for quenched alloy systems, in contrast to fluids, the mechanism of the encounters between growing droplets is important. Using the method outlined by LS, Davies *et al* [5] have discussed the effect of this mechanism. Then they concluded that with increasing droplet volume fraction the asymptotic scaling form of the droplet size distribution becomes flattened and more symmetric than that of LS [1] and Wagner [2] (LSW). Moreover, they found that this mechanism increases the growth rate, although the average droplet radius is still proportional to the cube root of the time.

Siggia [3] and Ohta [4] have shown that the Brownian coagulation is dominant for the droplet growth, except for in the region of small droplet volume fraction. However, they considered only ideal situations such as a monodisperse system. In the present letter we discuss more general situations, and moreover calculate explicitly the scaling function of the droplet size distribution function. For this purpose we use a similar technique to that of LS and Davies *et al* [5].

Let $f(v, t)$ be the droplet size distribution function per unit volume at time t, which describes the number of droplets that have volumes in the interval between v and $v + \mathrm{d}v$.

Following LS, the kinetic equation of $f(v, t)$ for the case including collision as well as the evaporation–condensation mechanism can be written as

$$(\partial/\partial t)f(v, t) = J_1(v) + J_2(v) \tag{1}$$

with

$$J_1(v) = -4\pi\alpha(\partial/\partial v)[(3v/4\pi)^{1/3}/R_c(t) - 1)f(v, t)] \tag{2}$$

$$J_2(v) = \tfrac{1}{2}\int_0^v c(v', v - v')f(v', t)f(v - v', t)\,\mathrm{d}v' - \int_0^\infty c(v, v')f(v', t)f(v, t)\,\mathrm{d}v' \tag{3}$$

where α is the capillary length, $R_c(t)$ the critical droplet radius to be determined on the basis of the conservation law for the total droplet volume, and $c(v_1, v_2)$ the collision frequency factor for collisions between two droplets of volumes v_1 and v_2. The term J_1 denotes the evaporation–condensation mechanism, and J_2 the collision. The form of $c(v_1, v_2)$ depends on the mechanism of collision [6–8]. For the encounter mechanism, LS showed that $c(v_1, v_2)$ is proportional to $v_1 + v_2$. For Brownian coagulation, it was shown by Smoluckowski [6] to be

$$c(v_1, v_2) = \beta(v_1^{1/3} + v_2^{1/3})(v_1^{-1/3} + v_2^{-1/3}) \tag{4}$$

$$\beta = 4k_B T/5\eta \tag{5}$$

where $k_B T$ is the usual thermal energy and η the shear viscosity. To obtain the above kinetic equation we have assumed that (i) the collision takes place instantaneously to form a larger droplet whose volume is the sum of the volumes of coagulated droplets, (ii) the collision occurs only between two droplets (the binary collision approximation), and (iii) the many-body effect beyond the LSW mean-field approximation is neglected as the first theoretical step and thus the critical radius $R_c(t)$ is replaced by the average radius $\bar{R}(t)$, defined by

$$\bar{R}(t) \equiv \int_0^\infty (3v/4\pi)^{1/3}f(v, t)\,\mathrm{d}v \Big/ \int_0^\infty f(v, t)\,\mathrm{d}v. \tag{6}$$

Now we discuss the asymptotic behaviour of (1)–(4). We assume the following scaling form of $f(v, t)$ [4]:

$$f(v, t) = Q\bar{v}(t)^n F(x) \tag{7}$$

with

$$Q = \int_0^\infty vf(v, t)\,\mathrm{d}v \tag{8}$$

$$\bar{v}(t) = \int_0^\infty vf(v, t)\,\mathrm{d}v \Big/ \int_0^\infty f(v, t)\,\mathrm{d}v \tag{9}$$

$$x = v/\bar{v}(t). \tag{10}$$

The requirement that the droplet volume fraction, Q, is independent of time leads to

$$n = -2 \tag{11}$$

together with

$$\int_0^\infty xF(x)\,\mathrm{d}x = 1. \tag{12}$$

We also have a normalisation condition from (7) and (9):

$$\int_0^\infty F(x)\,\mathrm{d}x = 1. \tag{13}$$

Then, in terms of $F(x)$ and $\bar{v}(t)$, equations (1)–(3) are rewritten as

$$[2F(x) + x(\mathrm{d}/\mathrm{d}x)F(x)](\mathrm{d}/\mathrm{d}t)\bar{v}(t) = 4\pi\alpha j_1(x) - \beta Q j_2(x) \tag{14}$$

with

$$j_1(x) = (\mathrm{d}/\mathrm{d}x)[(x^{1/3}/a - 1)F(x)] \tag{15}$$

$$j_2(x) = \tfrac{1}{2}\int_0^x c'(y, x-y)F(y)F(x-y)\,\mathrm{d}y - \int_0^\infty c'(x,y)F(x)F(y)\,\mathrm{d}y \tag{16}$$

$$c'(x, y) = c(x, y)/\beta \tag{17}$$

$$a = \int_0^\infty x^{1/3}F(x)\,\mathrm{d}x. \tag{18}$$

Here we should note that from (6) and (9) we have

$$(4\pi/3)\bar{R}(t)^3 = a^3\bar{v}(t). \tag{19}$$

Integrating (14) with respect to x from 0 to ∞, we find the growth equation of the average size:

$$(\mathrm{d}/\mathrm{d}t)\bar{v}(t) = 4\pi\alpha(ehQ + F(0)) \tag{20}$$

with

$$e = \beta/4\pi\alpha \tag{21}$$

$$h = 2(1 + ab) \tag{22}$$

$$b = \int_0^\infty x^{-1/3}F(x)\,\mathrm{d}x. \tag{23}$$

Following the estimation by Ohta [4] we set $e = 4/\pi$. Inserting (20) into (14) we finally obtain the closed equation for $F(x)$:

$$F(x) + (\mathrm{d}/\mathrm{d}x)(G(x)F(x)) = -(4/\pi)gQj_2(x) \tag{24}$$
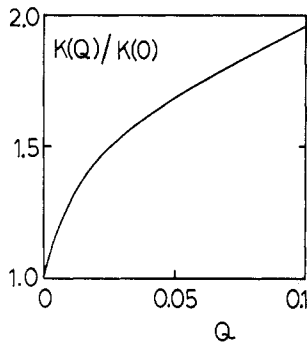
with

$$G(x) = -(x^{1/3}/a - 1)g + x \tag{25}$$

Figure 1. The relative growth rate, $K(Q)/K(0)$, as a function of Q with $K(0) = (4/9)\alpha$.

$$g = 1/(4hQ/\pi + F(0)). \tag{26}$$

These equations are mathematically analogous to those discussed by Davies *et al* [5]. We can thus solve (24) subject to conditions (12) and (13) by using the same iteration method. Hence, we shall quote only the final result, omitting intermediate calculations. The following results are obtained for each value of Q from 20 iterations, as was outlined in section 2.6 of [5].

The function $F(x)$ is convenient for calculation, but not for comparison with experiments. Since what is usually measured is the linear droplet dimension, we need to convert $F(x)$ into a linear droplet size distribution function. As was discussed in [5], the normalised scaling function for the linear droplet size, $p(r)$, is given by

$$p(r) = 3ax^{2/3}F(x) \tag{27}$$

$$r = x^{1/3}/a \tag{28}$$

where r is the linear droplet size divided by the average one, $\bar{R}(t)$. From (19) and (20) the average droplet radius, $\bar{R}(t)$, is found to grow as

$$\bar{R}(t)^3 - \bar{R}(0)^3 = K(Q)t \tag{29}$$

where $\bar{R}(0)$ is the initial average droplet radius, and $K(Q)$ the Q-dependent growth rate given by

$$K(Q) = 3\alpha a^3[(4/\pi)hQ + F(0)]. \tag{30}$$

We should remark that in the dilute limit $Q \to 0$ with $K(0) = (4/9)\alpha$ from (24) and (30) we can recover the LSW theory. Numerical results for $K(Q)$ and $p(r)$ are shown as functions of Q in figures 1 and 2, respectively. In figure 3 we show the standard deviation, σ, and the skewness, k_s, of $p(r)$ for each value of Q.

In summary, we have studied the effect of Brownian coagulation on the Ostwald ripening. With increasing droplet volume fraction, the growth rate $K(Q)$ increases and the scaling function $p(r)$ broadens, while the temporal power laws still hold. These results are similar to those for the encounter mechanism. However, in contrast to the case for encounters, the scaling function in the present case becomes positively skew, even though Q is small. This tendency is in good agreement with recent experimental results [9]. The detailed comparison of the present results with the experimental results as well as previous theories will be discussed elsewhere.
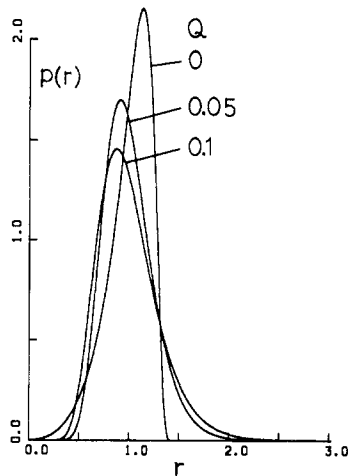
Figure 2. The scaling function $p(r)$ against r for $Q = 0$ (the LSW theory), 0.05, and 0.1.
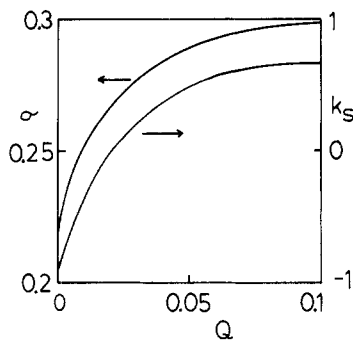
Figure 3. The standard deviation, σ, and the skewness, k_s, of $p(r)$ as a function of Q with $\sigma = 0.215$ and $k_s = -0.911$ at $Q = 0$.

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