

# Droplet interaction in the spinodal decomposition of a fluid

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The interaction between a pair of non-Brownian droplets in the spinodal decomposition of a binary fluid is examined. The interaction arises due to the convective term in the model H momentum equation, which is reciprocal to the convective term in the concentration equation. The dominant contribution to this convective term is due to the interface between the droplet and the matrix, where concentration gradients are large, and this contribution is determined in the limit where the distance between the droplets  $L$  is large compared to the radius of a droplet  $R$ . The force on the fluid due to the interfacial concentration gradient is first calculated, and it is found that there is a net force on the fluid only if there is a deviation of the interfacial concentration profile from the equilibrium profile. This deviation is related to the flux of solute at the interface, which is calculated correctly to  $(R/L)^2$  for the interacting droplets. The average velocity of the droplets is then calculated by solving the momentum equations for the system. It is found that the interaction between the droplets does cause a spontaneous motion of the droplets towards each other. © 1998 American Institute of Physics. [S0021-9606(98)50741-6]

## I. INTRODUCTION

It has been known for some time, both experimentally<sup>1</sup> and theoretically<sup>2-4</sup> that the dynamics of spinodal decomposition and droplet coarsening in fluids could be very different from that in solid alloys; this has been confirmed by more recent experimental<sup>5,6</sup> and computer simulation<sup>7,8</sup> studies. The coarsening process in solid alloys proceeds by diffusion of the molecules along a solid lattice, but in a fluid convective transport could enhance the coarsening process. The dynamics of spinodal decomposition could be distinguished into two types; the coarsening due to the motion of random interfaces forming a bicontinuous pattern in a symmetric quench, and the growth of droplets in an off-symmetric quench. The coarsening of droplets is considered to be due to two possible mechanisms:

- (1) The diffusion mechanism,<sup>9,10</sup> which involves the growth of droplets with radius larger than a critical value and the shrinking of droplets with radius smaller than this value due to diffusion of the dispersed phase through the matrix;
- (2) The coagulation mechanism,<sup>2,11</sup> where droplets of different sizes undergoing Brownian motion collide and coalesce to give a larger droplet.

The former mechanism is observed when the droplet density is relatively low so that there are no collisions between droplets, while the latter is observed when the droplet density is higher. In both cases, the mean radius of the droplets obeys a scaling law of the form  $R(t) \propto t^{1/3}$ . The scaling law is the same that for the Lifshitz-Slyozov<sup>9,10</sup> theory for alloys, but it has experimentally been observed that the rate of growth of the average radius could be much larger than that in an alloy.

However, recent experiments<sup>5,6</sup> have suggested that there is another mechanism, apart from Brownian motion,

which could lead to coalescence of droplets. In these experiments, it was observed that even when the droplets are sufficiently large that Brownian motion is negligible, coalescence takes place due to the spontaneous motion of droplets towards each other. The author suggested that this could be due to the force exerted by the convective term in the momentum conservation equation, which is the reciprocal of the term in the convective transport term in the mass conservation equation in the model H<sup>12</sup> equations for a binary fluid. Further, it was also suggested that this force is caused by the sharp gradient in the concentration at the droplet interface. An analysis of the motion of a droplet in a steady concentration gradient was carried out by Tanaka<sup>13</sup> to illustrate the effect of concentration gradient on droplet motion.

In this analysis, the motion of a pair of droplets is determined in the limit where the distance of separation  $L$  is large compared to the radius of the droplet  $R$ . The model H momentum equation, which contains a term reciprocal to the convective term in the concentration equation, is used to determine the velocity field. The velocity induced in the fluid due to a moving interface is determined using the assumption that the interfacial thickness is small compared to the radius of the droplets. The calculation shows that an equilibrium interface does not exert any force on the fluid, but nonequilibrium corrections to the interfacial concentration profile could result in a force due to the convective term in the model H momentum equation. The motion of the interface is then related to the flux of solute at the interface, which is asymmetric due to the interaction between the droplets. The diffusion flux correct to  $O(R/L)^2$  is calculated, and the velocity of the droplet due to the convective term in the momentum equation is determined.

## II. ANALYSIS

The momentum equation for the velocity field in a binary fluid contains an additional term, reciprocal to the con-

vective term in the concentration equation, which could result in a fluid velocity driven by concentration gradients. For an incompressible fluid, the momentum equation in the absence of inertial effects is<sup>12</sup>

$$\partial_j \sigma_{ij} + \left[ \partial_i c \frac{\delta E}{\delta c} \right]_{\perp} = 0, \quad (1)$$

where indicial notation has been used to represent vectors, and  $\partial_i \equiv (\partial/\partial x_i)$ , and  $[\ ]_{\perp}$  represents the transverse projection operator. In Eq. (1), the thermal noise is neglected for simplicity, because the issue of interest is the systematic fluid velocity induced by the convective force density, which is the second term on the left-hand side of Eq. (1). The transverse part of the stress tensor,  $\sigma_{ij}$ , is given by Newton's law for a simple fluid with viscosity  $\eta$ ,

$$\sigma_{ij} = \eta(\partial_i v_j + \partial_j v_i), \quad (2)$$

and  $E$  is the free energy given by the Cahn–Hilliard expression with an additional contribution due to the kinetic energy of the fluid

$$E = \int d\mathbf{x} \left[ f[c] + \frac{K}{2} \partial_i^2 c + \frac{\rho}{2} v_i^2 \right]. \quad (3)$$

With the above definition of the free energy, the momentum conservation equation (1) can easily be solved to determine the velocity field in the fluid induced by concentration gradients. For a Newtonian fluid, the velocity field is

$$v_i(\mathbf{x}) = \int d\mathbf{x}' J_{ij}(\mathbf{x} - \mathbf{x}') \left[ \partial_j c \frac{\delta E}{\delta c} \right], \quad (4)$$

where  $J_{ij}(\mathbf{x} - \mathbf{x}')$  is the Oseen tensor

$$J_{ij}(\mathbf{x} - \mathbf{x}') = \frac{1}{8\pi\eta} \left[ \frac{\delta_{ij}}{|\mathbf{x} - \mathbf{x}'|} + \frac{(x_i - x'_i)(x_j - x'_j)}{|\mathbf{x} - \mathbf{x}'|^3} \right]. \quad (5)$$

There are two contributions to the force density ( $\partial_j c (\delta E/\delta c)$ ), one due to the square gradient term and the other due to the variation in free energy with concentration  $f[c]$ . The term proportional to  $f[c]$  does not result in flow, since it results in a longitudinal contribution to the force density,

$$\partial_i c \frac{\delta f[c]}{\delta c} = \partial_i (f[c]). \quad (6)$$

The transverse component of the velocity field due to this contribution to the force density is

$$\int d\mathbf{x}' J_{ij}(\mathbf{x} - \mathbf{x}') \partial_j (f[c]) = \int d\mathbf{x}' \partial'_j (J_{ij}(\mathbf{x} - \mathbf{x}') f[c]), \quad (7)$$

where  $\partial'_j \equiv (\partial/\partial x'_j)$ . In the above equation, the identity  $\partial_j J_{ij}(\mathbf{x} - \mathbf{x}') = 0$  has been used. Equation (7) reduces to a surface integral, which is zero because the concentration field decreases to a constant value far from the droplets. Consequently, there is no contribution to the convective force density due to the term proportional to  $f[c]$  in the expression for the free energy.

Consequently, the only contribution to the fluid velocity field is due to the square gradient contribution to the free energy, and the velocity field is given by

$$v_i(\mathbf{x}) = -K \int d\mathbf{x}' J_{ij}(\mathbf{x} - \mathbf{x}') [\partial_j c \partial_k^2 c]. \quad (8)$$

In order to simplify Eq. (8) for the velocity profile, it is useful to determine the expression  $\partial_j c \partial_k^2 c$  in a spherical coordinate system with origin at the center of the droplet. For an axisymmetric concentration field,

$$\partial_j c = \left( n_j \frac{\partial c}{\partial r} + t_j \frac{1}{r} \frac{\partial c}{\partial \theta} \right), \quad (9)$$

$$\partial_k^2 c = \left( \frac{\partial^2 c}{\partial r^2} + \frac{2}{r} \frac{\partial c}{\partial r} + \frac{1}{r^2 \sin(\theta)} \frac{\partial}{\partial \theta} \sin(\theta) \frac{\partial c}{\partial \theta} \right), \quad (10)$$

where  $\mathbf{n}$  and  $\mathbf{t}$  are the unit vectors in the  $r$  and  $\theta$  directions, and  $\theta$  is the azimuthal angle. Since the concentration gradients are sharp only near the interface, it is useful to express the concentration field in terms of the dimensionless coordinate  $z^* = (r - R)/h$ , where  $h$  is the interfacial thickness discussed a little later,

$$\partial_j c = \left( e_{rj} \frac{1}{h} \frac{\partial c}{\partial z^*} + e_{\theta j} \frac{1}{R + h z^*} \frac{\partial c}{\partial \theta} \right), \quad (11)$$

$$\begin{aligned} \partial_k^2 c = & \left( \frac{1}{h^2} \frac{\partial^2 c}{\partial z^{*2}} + \frac{1}{h(R + h z^*)} \frac{\partial c}{\partial z^*} \right. \\ & \left. + \frac{1}{(R + h z^*)^2} \frac{1}{\sin(\theta)} \frac{\partial}{\partial \theta} \sin(\theta) \frac{\partial c}{\partial \theta} \right). \end{aligned} \quad (12)$$

In the above expression, it is easy to see that the that in the expression for  $\partial_j c$ , the gradient in the  $\theta$  direction, which is the coefficient of  $t_j$ , is  $O(h/R)$  smaller than the gradient in the  $r$  direction proportional to  $n_j$ . Consequently, the contribution to  $\partial_j c$  proportional to  $t_j$  is neglected in the leading approximation. In the expression for  $\partial_k^2 c$ , the derivative in the  $\theta$  direction provides the smallest contribution, and consequently only the first two terms representing gradients in the  $r$  direction are retained. In the limit  $h \ll R$ , the volume integral in the expression for the velocity (4) can be written as

$$v_i(\mathbf{x}) = \int dA J_{ij}(\mathbf{x} - \mathbf{x}_s) n_j(\mathbf{x}_s) G(\mathbf{x}_s), \quad (13)$$

where  $A$  is the area of the interface,  $\mathbf{x}_s$  is the position vector along the interface, and  $\mathbf{n}$  is the outward unit normal to the droplet. The magnitude of the force per unit area,  $G(\mathbf{x}_s)$ , is

$$\begin{aligned} G(\mathbf{x}_s) = & -\frac{K}{h^2} \int_{-\infty}^{\infty} dz^* \left[ \partial_{z^*} c \left( \partial_{z^*}^2 c + \frac{h}{(R + h z^*)} \partial_{z^*} c \right) \right] \\ = & -\frac{K}{h^2} \left[ \frac{(\partial_{z^*} c)^2}{2} \right]_{-\infty}^{\infty} - \frac{2K}{R h} \int_{-\infty}^{\infty} dz^* (\partial_{z^*} c)^2. \end{aligned} \quad (14)$$

In deriving the second expression above, a term proportional to  $(h/R)$  has been neglected in the denominator of the second term on the right-hand side. For a system at equilibrium,

the first term on the right-hand side of Eq. (14) is zero because the concentration gradient is zero at large distances from the interface. Consequently, the dominant nonzero contribution is due to the second term on the right-hand side, which is the product of the curvature ( $2/R$ ) and the surface tension ( $K/h^2$ )  $\int_{-\infty}^{\infty} (\partial_{z^*} c)^2$ , in agreement with the theory of Kawasaki and Ohta.<sup>14</sup> Note the negative sign because the surface tension acts in a direction opposite to the outward unit normal at the surface. For a system which is not at equilibrium, there is a nonzero contribution due to the first term on the right-hand side of Eq. (14), since the flux could be nonzero at the interface. Moreover, this term is the dominant contribution to the force density, since it is  $(R/h)$  larger than the second term. Consequently, the convective force density due to this term is considered in the remainder of the analysis.

The fluid flow due to departure from equilibrium is calculated for a specific model of the interface

$$f[c] = \frac{\chi}{2} (c - c_d)^2 (c - c_m)^2, \quad (15)$$

where  $\chi$  is a constant. The departure from equilibrium is caused by the diffusional flux of the solute from the matrix to the droplet. It is assumed that the concentration of the droplet has attained its equilibrium value, while the flux is due to the gradient in concentration in the matrix. The flux of material causes the motion of the interface along its unit normal, and the concentration at any point in a reference frame fixed on the interface is determined from the equation

$$\begin{aligned} -u(\mathbf{x}_s) \partial_z c &= \Lambda \partial_z^2 \left[ \frac{\delta E}{\delta c} \right] \\ &= \Lambda \partial_z^2 [-K \partial_z^2 c + 2\chi(c - c_d) \\ &\quad \times (c - c_m)(2c - c_d - c_m)], \end{aligned} \quad (16)$$

where  $u(\mathbf{x}_s)$  is the velocity of the interface at the point  $\mathbf{x}_s$ , and  $\Lambda$  is the Onsager transport coefficient. The velocity  $u(\mathbf{x}_s)$  is related to the diffusion flux of solute at the interface a little later.

The equilibrium concentration of the interface is

$$c_e = \frac{c_d + c_m}{2} - \frac{c_d - c_m}{2} \tanh\left(\frac{z}{h}\right), \quad (17)$$

where  $h = [((c_d - c_m)^2/4)(\chi/K)]^{-1/2}$  is the interfacial thickness,  $c_d$  is the concentration in the droplet, and  $c_m$  is the concentration in the matrix. In the above calculation, curvature effects have been neglected while determining the interfacial concentration since it is assumed that the radius of curvature is large compared to the interfacial thickness. It is useful to express the interfacial concentration as  $c = \psi(c_d - c_m)/2 + (c_d + c_m)/2$ , where  $\psi$  is now a dimensionless concentration field. The equilibrium concentration  $\psi_e$  in the interface is

$$\psi_e = -\tanh(z/h). \quad (18)$$

The nonequilibrium correction to the concentration is determined using an expansion in the departure from equilibrium  $\phi = (\psi - \psi_e)$ . Equation (16) correct to linear order in the departure from equilibrium  $\phi$  is

$$-\frac{u(\mathbf{x}_s)}{h} \partial_{z^*} \psi_e = \frac{D}{h^2} \partial_{z^*}^2 \left[ -\frac{1}{4} \partial_{z^*}^2 \phi + \left( \frac{3\psi_e^2 - 1}{2} \right) \phi \right], \quad (19)$$

where the dimensionless coordinate  $z^* = (z/h)$ , and  $D = \Lambda \chi (c_d - c_m)^2$  is the bulk diffusion coefficient. The above fourth order equation can be integrated twice to obtain

$$\begin{aligned} &\left[ -\frac{1}{4} \partial_{z^*}^2 \phi + \left( \frac{3\psi_e^2 - 1}{2} \right) \phi \right] \\ &= \frac{uh}{D} \left[ \int_0^{z^*} dy (-\psi_e(y)) + z^* - \log(2) \right], \end{aligned} \quad (20)$$

where the constants of integration are determined from the requirement that the  $\phi = 0$  and  $d_{z^*} \phi = 0$  in the droplet phase  $z^* \rightarrow -\infty$ , where the concentration is equal to the equilibrium concentration. It turns out to not be necessary to obtain the numerical solution to Eq. (20) for  $\phi$ , since the function  $G(\mathbf{x}_s)$  can be determined from the boundary conditions alone. It is sufficient to recognize the following limiting behavior of the function  $\phi(z^*)$ :

$$\begin{aligned} \phi &\propto \exp(2z^*) \quad \text{for } z^* \rightarrow -\infty, \\ \phi &= \frac{2u(\mathbf{x}_s)h}{D} z^* \quad \text{for } z^* \rightarrow \infty. \end{aligned} \quad (21)$$

The function  $G(\mathbf{x}_s)$  can now be determined as follows:

$$\begin{aligned} G(\mathbf{x}_s) &= \frac{-K(c_d - c_m)^2}{4h^2} \int_{-\infty}^{\infty} dz^* \partial_{z^*} \psi \partial_{z^*}^2 \psi \\ &= \frac{-K(c_d - c_m)^2}{8h^2} (\partial_{z^*} \psi)^2 \Big|_{-\infty}^{\infty} \\ &= - \left( \frac{K(c_d - c_m)^2 u(\mathbf{x}_s)^2}{2D^2} \right). \end{aligned} \quad (22)$$

The convective force per unit area of the interface is a function of the velocity of the interface  $u(\mathbf{x}_s)$ . The velocity  $v_i(\mathbf{x})$  due to the convective force is determined by carrying out the integral over the surface of the droplets in Eq. (13). The most convenient method for determining this integral involves expanding the Oseen tensor  $J_{ij}(\mathbf{x} - \mathbf{x}_s)$  about its value at the center of the droplet

$$\begin{aligned} v_i(\mathbf{x}) &= J_{ij}(\mathbf{x} - \mathbf{x}_c) \int dA n_j(\mathbf{x}_s) G(\mathbf{x}_s) + \partial_k J_{ij}(\mathbf{x} - \mathbf{x}_c) \\ &\quad \times \int dA r_k n_j(\mathbf{x}_s) G(\mathbf{x}_s) + \partial_k \partial_l J_{ij}(\mathbf{x} - \mathbf{x}_c) \\ &\quad \times \int dA r_k r_l n_j G(\mathbf{x}_s) + \dots, \end{aligned} \quad (23)$$

where  $\mathbf{x}_c$  is the position of the center of the droplet and  $\mathbf{r} = \mathbf{x}_s - \mathbf{x}_c$ . It can easily be verified that if the function  $G(\mathbf{x}_s)$  is independent of position on the droplet surface, the fluid velocity is zero at all points as follows:

- (1) All terms proportional to  $\int dA n_j, \int dA n_j r_k r_l, \dots$  are zero because the integrands are odd functions of the unit normal to the interface.
- (2) The term  $\partial_k J_{ij}(\mathbf{x} - \mathbf{x}_c) \int dA n_j r_k$  is proportional to  $\partial_j J_{ij}(\mathbf{x} - \mathbf{x}_c)$ , which is zero due to incompressibility. In a similar manner, all higher order terms proportional to  $\int dA n_j r_k r_l r_m, \dots$  are also zero.

However, if there is a variation in the velocity  $u$  along the surface of the droplet,  $v_i$  could be nonzero. One mechanism for this variation is the interaction between two droplets, where the concentration field due to the presence of one droplet affects the concentration field around the other. For example, consider two droplets of radius  $R$  separated by a distance  $L$ . Two coordinate systems,  $\mathbf{x}_A$  and  $\mathbf{x}_B$ , with origins at the centers of the two droplets, are chosen for the analysis, and the vector distance from droplet  $B$  to droplet  $A$  is  $\mathbf{L}$ . It is convenient to write equations for the reduced concentration  $c$ , which is the difference between the local concentration and the average concentration in the matrix, so that the boundary condition is  $c \rightarrow 0$  for  $r \rightarrow \infty$  in the matrix. A multipole expansion is used to determine the concentration field in the limit  $R \ll L$ , and the terms in the expansion are chosen to satisfy the condition  $c = -c_s$ , at the surface of the droplet, where  $c_s$  is the difference between the concentration in the matrix at  $r \rightarrow \infty$  and the equilibrium concentration of the matrix phase at the surface of the droplet. The concentration field around the droplets, correct to  $(R/L)^2$ , is

$$c = \frac{-c_s R}{r_A} \left( 1 - \frac{R}{L} + \frac{R^2}{L^2} \right) - \frac{c_s R}{r_B} \left( 1 - \frac{R}{L} + \frac{R^2}{L^2} \right) - \frac{c_s R^4 L_j}{L^3} \left( \frac{x_{Aj}}{r_A^3} - \frac{x_{Bj}}{r_B^3} \right). \quad (24)$$

The flux at the surface of droplet  $A$ , correct to  $(R/L)^2$ , is

$$J_{Ai}|_{r_A=R} = -D \partial_i c|_{r_A=R} = \frac{-D c_s x_{Ai}}{R^2} \left( 1 - \frac{R}{L} + \frac{R^2}{L^2} + \frac{3R x_{Aj} L_j}{L^3} \right). \quad (25)$$

The normal velocity of the surface is

$$u(\mathbf{x}_s) = - \frac{J_{Ai} n_{Ai}}{(c_d - c_m)} = \frac{D c_s}{R(c_d - c_m)} \left( 1 - \frac{R}{L} + \frac{R^2}{L^2} \right) + \frac{3D c_s x_{Aj} L_j}{L^3(c_d - c_m)}. \quad (26)$$

The fluid velocity is proportional to the square of  $u(\mathbf{x}_s)$ , which is

$$[u(\mathbf{x}_s)]^2 = \left( \frac{D c_s}{R(c_d - c_m)} \right)^2 \left[ \left( 1 - \frac{R}{L} + \frac{R^2}{L^2} \right)^2 + \frac{6R x_{Aj} L_j}{L^3} \left( 1 - \frac{R}{L} + \frac{R^2}{L^2} \right) + \left( \frac{3R x_{Aj} L_j}{L^3} \right)^2 \right]. \quad (27)$$

In the above expression, the first term on the right-hand side does not contribute to the fluid velocity  $v_i$  for reasons given above. The third term on the right-hand side is proportional to  $(R/L)^4$ , which is small compared to the  $(R/L)^2$  dependence of the second term in the limit  $L \gg R$ . Consequently, we examine the effect of the second term on the motion of droplet  $A$ . The fluid velocity at the surface of droplet  $A$  contains two contributions, one due to the interface of droplet  $A$  and the other due to the interface of droplet  $B$ . It can easily be verified that the contribution due to the interface of droplet  $B$  is  $O(R/L)$  smaller than that due to the interface of droplet  $A$ . Consequently, while calculating the velocity of droplet  $A$ , it is sufficient to consider the surface of droplet  $A$  alone. The velocity of the fluid at the surface of droplet  $A$  is

$$v_i = \frac{-3K c_s^2 L_k}{L^3} \int d\mathbf{x}'_A J_{ij}(\mathbf{x}_A - \mathbf{x}'_A) n_j(\mathbf{x}') \frac{x'_{Ak}}{R}, \quad (28)$$

where  $\mathbf{x}_A$  and  $\mathbf{x}'_A$  are points on the surface of droplet  $A$ . The velocity of the droplet  $V_{Ai}$  can be determined by carrying out an integral over the radius of this droplet,

$$V_{Ai} = \frac{1}{4\pi R^2} \int d\mathbf{x}_A v_i. \quad (29)$$

The integral in Eq. (29) can easily be carried out to obtain the following expression correct to leading order in  $(R/L)$ ,

$$V_{Ai} = \frac{-2K c_s^2 R L_i}{3\eta L^3}. \quad (30)$$

A similar calculation can be carried out for the average velocity of droplet  $B$ , and it can be shown that the average velocity is

$$V_{Bi} = \frac{2K c_s^2 R L_i}{3\eta L^3}. \quad (31)$$

The above results indicate that the convective term in the model H momentum equation gives rise to a spontaneous motion of the droplets towards each other, since  $\mathbf{L}$  is the vector directed from the center of droplet  $B$  to the center of droplet  $A$ .

It is important to note at this point that the spontaneous motion of the droplets is driven not by a variation in the shape from its equilibrium spherical shape, but due to an asymmetry in the flux at the interface. A spherically symmetric concentration field around a droplet cannot induce a transverse velocity component, as evident from the discussion after Eq. (23). However, when there is an interaction between the concentration fields around two droplets, the flux at the surface of a droplet is not spherically symmetric.

Due to this, the convective force density [in Eq. (13)] is not spherically symmetric, and there is a transverse velocity field even if the droplet is spherical.

### III. CONCLUSIONS

It is useful to qualitatively summarize the various steps in the present analysis. The interaction between a pair of droplets in a binary fluid due to convective effects at the interface was analyzed. The convective effects arise from a term in the momentum equation for the fluid which is reciprocal to the convective term in the concentration equation, and this term is required to ensure that the coupled concentration and momentum terms satisfy the Poisson bracket relations. It was shown that the contribution of this term to the transverse component of the velocity is proportional to the product of the first and second spatial gradients of the concentration profiles, which are large at the interface between the droplet and the matrix. Consequently, the dominant contribution to this convective term is due to the large concentration gradients at the interface.

The inertial terms in the momentum equation were neglected, and the velocity at any point in a viscous flow is expressed as an volume integral of the product of the fluid mobility and the forces density at other points. The analysis was carried out for the case where the interface thickness is small compared to the radius of the droplet, and so the volume integral of the force density could be reduced to the product of integrals over the coordinate normal to the interface and the surface area of the droplet. The interfacial concentration profile was determined using a diffusion equation for the concentration field, with the free energy given by the Cahn–Hilliard square gradient expression for a regular solution. It was shown that an equilibrium interfacial concentration profile does not cause any fluid flow, but there could be flow due to deviations of the concentration profile from its equilibrium value. While calculating the deviation from equilibrium, it was assumed that the concentration in the droplet is equal to the equilibrium concentration, but there is a concentration gradient in the matrix which causes a flux of solute from the matrix to the droplet. Using the relation between the flux of solute and the motion of the interface, the convective force density per unit area of the interface was related to the flux of solute at the interface.

The fluid velocity was then determined by integrating the product of the mobility and the force density per unit area over the interface of the droplet. It was found that if the flux is constant on the surface of the droplet, the total fluid velocity is identically zero. However, if there is an interaction between the concentration fields of two droplets, the flux at the interface is not symmetric and this could result in a non-

zero fluid velocity. The flux at a point on the interface of a droplet which is facing the second droplet is lower than that at a point not facing the other droplet, and this difference results in a fluid flow which tends to bring the droplets towards each other along their line of centers. It is interesting to note that if a similar calculation is done for a solid alloy, the same difference in flux would cause the droplets to move away from each other due to the greater accumulation of material at points not facing the second droplet.

The above calculation indicates that the convective effect does result in the spontaneous motion of the droplets towards each other, and this could result in the coalescence of the droplets. There are two requirements for spontaneous motion;

- (1) The deviation of the interfacial profile from the equilibrium profile due to the flux of solute at the interface;
- (2) The variation of the flux at the interface due to the interaction between the droplets.

There have been various assumptions made in the above calculation. Since a multiple expansion has been used for the concentration field around interacting droplets, only terms  $O(R/L)^2$  smaller than the leading order term have been retained in the calculation. Consequently, the results would not be valid when the distance between the droplets is of the same magnitude as the droplet radius. In addition, the convective transport has been neglected while calculating the concentration field around the droplet. This is applicable only when the ratio  $(V_{Ai}R/D) \ll 1$ , or  $(Kc^2R^2/DL^2) \ll 1$ . Work is currently in progress to address these limitations. However, the calculation unambiguously indicates that there is a spontaneous motion of the droplets towards each other, as seen in experiments, due to the sharp concentrations at the interface.

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