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OSTWALD RIPENING OF PRECIPITATES AND IRREVERSIBLE PHENOMENA*

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OSTWALD RIPENING OF PRECIPITATES AND IRREVERSIBLE PHENOMENA*

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In principle, the manner according to which a phase transformation proceeds should be determinable by irreversible thermodynamics just as well as by appropriate kinetic equations embodying the transport of matter or energy. In practice, however, the former is seldom invoked and the latter approach provides the exclusive description of the transformation leaving one wondering what role the former plays. In this paper, the problem of Ostwald ripening of precipitates is studied to throw light on the underlying irreversible thermodynamics. From a path integral solution, it is shown that the size distribution evolves in such a manner that a Lagrangian is minimized. This Lagrangian is the sum of the dissipation potentials in the flux and force representations minus the rate of entropy production. The coarsening process proceeds in accordance with Onsager's principle of least dissipation. The implications of this study in relation to other irreversible phenomena are also discussed.

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Introduction

The phenomenon of Ostwald ripening of precipitates in a chemically closed system in which particles in a medium grow and dissolve continuously resulting in an increase with time of the average size and a corresponding decrease of the total number of particles has been described by several theories. Of these, the one put forward by Lifshitz and Slezov [1] and independently by Wagner [2] (to be denoted collectively as LSW) made a quantitative statement on the size distribution as a function of time. In this theory of LSW, the distribution function $N(r,t)$ for the size of a precipitate evolves with time t in accordance with the continuity equation

$$\frac{\partial N}{\partial t} = -\frac{\partial}{\partial r}(\dot{r}N) \quad . \qquad (1)$$

Assuming a growth law

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$$\dot{r} = v[r(t)] \tag{2}$$

for the individual particles, LSW obtained an asymptotic solution of Eqn. (1) for long time t. Kahlweit [3] later introduced a generalization of Eqn. (1) by allowing for fluctuation around the growth law (2). He rewrote the continuity equation as

$$\frac{\partial N}{\partial t} = -\frac{\partial}{\partial r}\{vN - \Theta\frac{\partial N}{\partial r}\} \quad , \tag{3}$$

where Θ is a measure of the mean-square fluctuation around the growth law (2).

In the following section, a path integral solution of Eqn. (3) will be presented treating Θ as a small parameter. In the limit $\Theta \to 0$, the solution becomes exact for Eqn. (1) of LSW.

Representation of Evolution Path

It is convenient to introduce the Green function [4] $G(r,t|r't')$ through the relation

$$N(r,t) = \int dr'\ G(r,t|r',t')N(r',t') \tag{4}$$

with

$$\lim_{t \to t'} G(r,t|r',t') = \delta(r - r') \quad . \tag{4a}$$

Given the size distribution $N(r',t')$ at time t', the green function enables one to obtain the size distribution $N(r,t)$ at a subsequent time t. The physical meaning of $G(r,t|r',t')$ is the fraction of particles of size r' at time t' that will evolve to particles of size r at time t.

If a given time interval $t_s - t_o$ is divided into infinitesimally small equal segments $t_s - t_{s-1}$, $t_{s-1} - t_{s-2}$, . . . $t_1 - t_o$, then after s iterations of Eqn. (4), we have

$$N(r_s,t_s) = \int dr_{s-1} \ldots \int dr_o W \begin{Bmatrix} r_s & r_{s-1} \ldots r_o \\ t_s & t_{s-1} \ldots t_o \end{Bmatrix} N(r_o,t_o) \quad , \tag{5}$$

where

$$W\begin{Bmatrix} r_s & r_{s-1} \ldots r_o \\ t_s & t_{s-1} \ldots t_o \end{Bmatrix} = G(r_s,t_s|r_{s-1},t_{s-1}) \cdot \ldots \cdot G(r_2,t_2|r_1,t_1)G(r_1,t_1|r_o,t_o) \quad . \tag{5a}$$

Bearing in mind the meaning of G, W may be regarded as the statistical weight of the particular evolution path that goes through sizes $r_o, r_1 \ldots r_s$ at times t_o, t_1 ... t_s.

Direct substitution of (4) into Eqn. (3) shows that G satisfies the same differential equation as $N(r,t)$. We write for reasons of bringing in an analogy

$$\Theta\frac{\partial G}{\partial t} = -\Theta\frac{\partial}{\partial r}(vG) + \Theta^2\frac{\partial^2 G}{\partial r^2} \quad . \tag{6}$$

Equation (6) has the same structure as the Schroedinger equation of a charged particle in the presence of an electromagnetic field with v playing the role of the vector potential and Θ that of the Planck's constant h [5]. This corresponding Schroedinger equation has [5], in the classical limit $h \to 0$, a solution of the form $\exp(i\phi/h)$, where the classical action ϕ has the asymptotic expansion $\phi = \phi_o + h\phi_1 + h^2\phi_2 + \ldots$.

By analogy, we write in the limit of small fluctuation, i.e., $\Theta \to 0$, a solution of Eqn. (6) in the form

$$G(r,t|r',t') = G_o \exp(-A/\Theta) \tag{7}$$

where G_o is a constant and $A = A(r,t|r',t')$ may be expanded in powers of Θ as

$$A = A_o + \Theta A_1 + \Theta^2 A_2 + \ldots \quad . \tag{7a}$$

Substituting (7) and (7a) into Eqn. (6) and equating equal powers of Θ, we find that the two lowest order terms in (7a) satisfy respectively

$$\frac{\partial A_o}{\partial t} + v\frac{\partial A_o}{\partial r} + \left(\frac{\partial A_o}{\partial r}\right)^2 = 0 \tag{8}$$

and

$$\frac{\partial A_1}{\partial t} + v\frac{\partial A_1}{\partial r} - \frac{\partial v}{\partial r} - \frac{\partial^2 A_o}{\partial r^2} + 2\frac{\partial A_o}{\partial r}\frac{\partial A_1}{\partial r} = 0 \quad . \tag{9}$$

Equations (8) and (9) have been solved [6] to obtain A and hence G. The results will be quoted here. We have

$$G(r_s,t_s|r_{s-1},t_{s-1}) \propto \exp\left\{-\int_{t_{s-1}}^{t_s} dt\left[L + \frac{\Theta}{2}\frac{\partial v}{\partial r}\right] / \Theta\right\} \quad , \tag{10}$$

where the Lagrangian is

$$L = \Phi + \Psi - \Gamma = (\dot{r} - v)^2/4 \tag{10a}$$

with

$$\Phi = \dot{r}^2/4 \quad , \tag{10b}$$

$$\Psi = v^2/4 \quad , \tag{10c}$$

$$\Gamma = \dot{r}\, v/2 \quad , \tag{10d}$$

and the restriction that L satisfies the Euler-Lagrange equation

$$\frac{\partial L}{\partial r} - \frac{d}{dT}\left(\frac{\partial L}{\partial \dot{r}}\right) = 0 \quad . \tag{11}$$

The Variational Principle

The physical significance of the results (10)-(11) will now be clarified. The second term in the integral of (10) may be dropped either for negligible fluctuation as in the original problem of LSW or asymptotically for long time t when the rate at which the growth rate changes with size becomes vanishingly small for both diffusion and reaction controlled processes. Because of the form of the Green function in (10), the statistical weight (5a) of an evolution path which is a product of the short-time Green functions, will then be just the exponentiation of the

action, i.e., the integral of the Lagrangian L over all the time segments. Equation (11) which represents extremization of this action leads to a family of admissible evolution paths of the form

$$\dot{r} = \sqrt{v^2 + c} \quad , \tag{12}$$

where c is an integration constant. Of these paths, the one that corresponds to the growth law (2) minimizes the Lagrangian L for all time t. This optimal path carries the most statistical weight in the evolution of the distribution function represented by Eqn. (5) although the other admissible paths also contribute.

Let us now examine the meaning of the three terms in the Lagrangian (10a). Treating r as a thermodynamic variable, the rate at which it relaxes towards equilibrium, i.e., the flux $\dot{r}$, is related to the conjugate thermodynamic force $\partial S/\partial r$ by

$$\dot{r} = \lambda \frac{\partial S}{\partial r} \tag{13}$$

where λ is a kinetic coefficient and S is the entropy of the system. Comparing with Eqn. (2), we have

$$v = \lambda \frac{\partial S}{\partial r} \quad . \tag{14}$$

Integrating Eqn. (14), we have for the change of entropy along an evolution path r(t)

$$\Delta S = \frac{1}{\lambda} \int dr v = \frac{1}{\lambda} \int dt(\dot{r}v) \quad . \tag{15}$$

Therefore, the rate of entropy production P is

$$P = \dot{S} = \dot{r}v/\lambda \quad . \tag{16}$$

The kinetic coefficient λ may be determined by comparing with results for the stationary state in which the distribution function loses its explicit dependence on time [so that Eqn (3) may be set zero] and is related to the entropy through the Boltzmann distribution $N[r(t)] \propto \exp\{S[r(t)]/k_B\}$, where k_B is the Boltzmann constant. It is straightforward to obtain

$$\lambda = \Theta/k_B \quad . \tag{17}$$

Since $\dot{r}$ is the flux and $v = \Theta\frac{\partial S}{\partial r}/k_B$ its conjugate thermodynamic force, we may, following Onsager, interpret Φ and Ψ in Eqns. (10b) and (10c) as dissipation potentials [7] in the flux and force representations, respectively. Together with Γ in Eqn. (10d) which represents the rate of entropy production, Φ and Ψ are measures of the degree of irreversibility and differ from one another only in the way of description of the nonequilibrium state.

Consider now a first order variation of L with respect to the flux $\dot{r}$ and the force $\frac{\partial S}{\partial r}$. We have

$$\begin{aligned} \delta L &= \frac{\partial L}{\partial \dot{r}} \delta \dot{r} + \frac{\partial L}{\partial(\frac{\partial S}{\partial r})} \delta(\frac{\partial S}{\partial r}) \\ &= \frac{1}{2}\left(\dot{r} - \frac{\Theta}{k_B}\frac{\partial S}{\partial r}\right)\delta\dot{r} + \frac{\Theta}{2k_B}\left(\frac{\Theta}{k_B}\frac{\partial S}{\partial r} - \dot{r}\right)\delta(\frac{\partial S}{\partial r}) \quad . \end{aligned} \tag{18}$$

For arbitrary variations of either the flux or the force, the first order change in L therefore remains zero so long as the deterministic growth law (2) is satisfied. The variational principle (18) is the same as Onsager's principle of least dissipation [7,8].

Discussion and Conclusion

From a path integral solution to the continuity equation, it is shown that the size distribution evolves in such a manner that an action integral or equivalently a Lagrangian is minimized. It is found that this Lagrangian is the sum of the dissipation potentials in the flux and force representations minus the rate of entropy production. Minimization of this Lagrangian by holding either the flux or the force constant leads to the conclusion that the underlying irreversible thermodynamic principle for the Ostwald ripening process as described by Eqns. (1) or (3) is the principle of least dissipation due originally to Onsager.

In view of our experience with classical mechanics that all natural paths in mechanical systems can be determined from the principle of least action, it is tempting to speculate whether a universal minimum principle also exists in transformation kinetics. This work sheds no light on this question and its associated controversies. However, Eqn. (3) has the structure of the Fokker-Planck equation which is used to describe the time evolution of a general class of irreversible phenomena [8]. Therefore, Onsager's principle should also be applicable to these phenomena subject to the condition that either fluctuation is small or the system is not far from a stationary or equilibrium state.

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