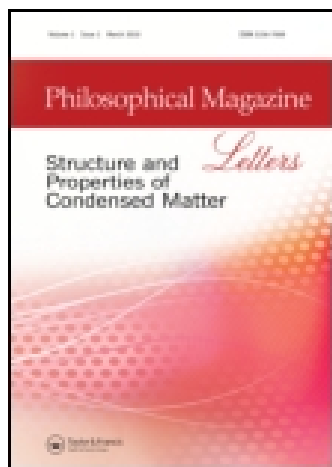


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Solid-state diffusion under a large driving force and the sintering of nanosized particles

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ABSTRACT

A nonlinear kinetic law and its corresponding variational principle are developed for solid-state diffusion under a large thermodynamic driving force. These are used to model the sintering of spherical particles. It is demonstrated that the classical linear diffusion law significantly underpredicts the sintering rate for nanosized particles.

§ 1. INTRODUCTION

It has often been assumed that the diffusive flux and the driving force for solid-state diffusion obey a linear relationship (Shewmon 1963). The linear kinetic law is, however, not valid if the thermodynamic driving force becomes very large. A typical example is the sintering of nanosized particles where a large driving force may exist. Hague and Mayo (1995) suggested an exponential driving force in their sintering model for nanosized particles. Campbell *et al.* (2002) noticed the same problem, although the main theme of their work was to demonstrate that the specific surface energy is no longer a constant for very small particles (less than 2.5 nm in diameter). These workers, however, did not re-examine the fundamentals of the diffusion law. In a textbook on electronic thin films, Tu *et al.* (1992) touched on the issue of large driving forces but did not study this further because their book deals mainly with small driving forces. In this paper we re-examine the kinetic law for solid-state diffusion under very large driving forces. A variational solution technique is developed for the nonlinear kinetic law and applied to the classical sintering problem. Many workers, including Johnson (1969), Coble (1970), Bouvard and McMeeking (1996) and Pan *et al.* (1998, 2003), have modelled sintering using linear kinetic laws. It is therefore an ideal problem to demonstrate the difference between the linear and the nonlinear kinetic laws.

§ 2. KINETIC LAW FOR LARGE DRIVING FORCE

We consider solid-state diffusion by the vacancy mechanism. For simplicity, we formulate the kinetic law in one dimension first and then extend it to higher dimensions later. Let J represent the atomic diffusion flux (number of atoms passing through a unit area per second), C_{atom} the atomic concentration (number of atoms per unit

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volume), V the atomic drifting velocity, f the atomic jumping frequency and a the atomic spacing. Then we have

$$J = C_{\text{atom}} V = C_{\text{atom}} af. \quad (1)$$

Let μ represent the chemical potential of an atom, which is the energy change on adding one atom to the solid from a 'zero-energy pool', and F the driving force acting on a single atom. We can write

$$F = -\frac{\partial\mu}{\partial x}. \quad (2)$$

If the driving force is zero, an atom can still exchange its position with a neighbouring vacancy by overcoming an energy barrier, known as the activation energy ΔG_m . The Boltzmann law states that the probability of finding an atom in a given position varies exponentially with the negative of the potential energy of that position divided by kT . The exchange frequency can be written as the product of an attempt frequency (the natural vibration frequency of the solid) and the probability of surmounting the barrier:

$$f_{F=0} = f_{\text{Debye}} \exp\left(\frac{-\Delta G_m}{kT}\right), \quad (3)$$

where k is the Boltzmann constant, T the absolute temperature and f_{Debye} the Debye frequency, which is a fundamental parameter of the solid (of the order of 10^{13} Hz for metals). The probability of finding a vacancy somewhere in the solid is given by

$$\frac{N_V^{\text{eq}}}{N_L} = \exp\left(\frac{-\Delta G_V}{kT}\right), \quad (4)$$

where ΔG_V is the formation energy of a vacancy, that is the energy change when we take an atom from inside the solid and put it on the surface (e.g. $N_V^{\text{eq}}/N_L \approx 10^{-4}$ for aluminium near its melting point of 660°C).

Diffusion occurs when a driving force F moves an atom in the direction of the force. Following Tu *et al.* (1992), the jumping frequency can be obtained as

$$f = 2 \frac{f_{F=0}}{n_c} \frac{N_V^{\text{eq}}}{N_L} \sinh\left(\frac{aF}{2kT}\right), \quad (5)$$

where n_c is the coordination number of an atom (number of nearest neighbours) and a is the atomic spacing. The diffusion flux is thus expressed as

$$J = C_{\text{solid}} af = C_{\text{solid}} 2 \left(a \frac{f_{F=0}}{n_c} \frac{N_V^{\text{eq}}}{N_L} \right) \sinh\left(\frac{aF}{2kT}\right).$$

Using the usual definition for the diffusion coefficient (Shewmon 1963):

$$D = a^2 \frac{f_{F=0}}{n_c} \left(\frac{N_V^{\text{eq}}}{N_L} \right) = a^2 \frac{f_{\text{Debye}}}{n_c} \exp\left(\frac{-\Delta G_m - \Delta G_V}{kT}\right) = D_0 \exp\left(\frac{-\Delta G_D}{kT}\right), \quad (6)$$

and noting that $C_{\text{atom}} = 1/\Omega$, where Ω is the atomic volume, we obtain the kinetic law

$$J = \frac{2D}{a\Omega} \sinh\left(\frac{aF}{2kT}\right) = \frac{2D}{a\Omega} \sinh\left(\frac{a}{2kT} \left(-\frac{\partial\mu}{\partial x}\right)\right). \quad (7)$$

If $aF \leq kT$, $\sinh(aF/2kT) \approx aF/2kT$, and then the nonlinear kinetic law is reduced to

the well-known linear law:

$$J = \frac{D}{kT\Omega} F = -\frac{D}{kT\Omega} \frac{\partial \mu}{\partial x}. \quad (8)$$

In three dimensions, the kinetic law (7) can be rewritten as

$$\mathbf{J} = \frac{2D}{a\Omega} \sinh\left(\frac{a|\mathbf{F}|}{2kT}\right) \frac{\mathbf{F}}{|\mathbf{F}|}, \quad (9)$$

where $\mathbf{F} = -\nabla\mu$. The formulation is completed by the well-known expressions for the chemical potential

$$\mu = -\Omega\sigma \quad (10)$$

at a grain boundary, where σ is the stress normal to the grain boundary, and

$$\mu = -\Omega\gamma_s\kappa, \quad (11)$$

at a free surface, where γ_s is the specific surface energy and κ the principal curvature of the free surface.

The above derivation of equations (6) and (7) contains many idealizations to the crystalline solid. In general, the diffusion coefficient D and the atomic spacing a in equations (7) and (9) should be treated as experimentally measured quantities.

§ 3. MAGNITUDE OF THE DRIVING FORCE

In order to illustrate the error caused by the linearization, $\sinh(aF/2kT) \approx aF/2kT$, we examine the magnitude of the term $aF/2kT$ for the sintering problem of two spherical particles under the framework of Coble's model. Coble (1970) assumed that boundary diffusion is the rate-controlling mechanism for sintering and used a linear diffusion law. Let R represent the radius of the particles, c the radius of the contact neck (the grain boundary) between the two particles, ρ the radius of curvature of the particles at the contact neck and y the shrinkage between the two particles. Coble assumed that radius of the curvature and the shrinkage are the same and proposed an approximate relationship between ρ , c and R which has been shown later to be valid using detailed numerical studies by Bouvard and McMeeking (1996) and Pan *et al.* (1998):

$$\rho = y = \frac{c^2}{4R}. \quad (12)$$

The chemical potential where the grain boundary meets the particle surface is given by

$$\mu = -\gamma_s\Omega\kappa = -\gamma_s\Omega\left(\frac{1}{\rho} - \frac{1}{c}\right) = -\gamma_s\Omega\left(4\frac{R}{c^2} - \frac{1}{c}\right), \quad (13)$$

and the driving force for grain-boundary diffusion can be estimated as

$$F = -\frac{\Delta\mu}{\Delta r} \approx -\frac{\mu - 0}{c/2} = 2\gamma_s(4R - c)\frac{\Omega}{c^3}. \quad (14)$$

Using $a = 0.5$ nm, $\gamma_s = 1$ J m⁻², $\Omega = 0.02$ nm³ and $T = 1160$ K, which is half the melting temperature of alumina, figure 1 shows the ratio of $[\sinh(aF/2kT)]/(aF/2kT)$ as a function of c/R for a range of values of particle radius R . From the figure it is evident that the linearization causes huge errors in calculating the driving

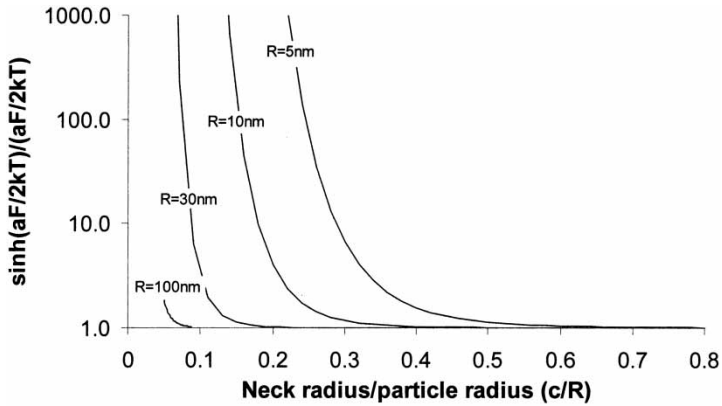


Figure 1. Ratio of $[\sinh(aF/2kT)]/(aF/2kT)$ for the sintering of two particles as a function of the ratio between the neck size c and the particle radius R .

force over a wide range of c/R for particles of radius $R \leq 30$ nm. For particles with $R \geq 100$ nm, however, the linearization is generally acceptable. A unique feature of the nonlinear kinetic law is that an atomic length scale, a , enters the equation.

§ 4. VIRTUAL POWER AND VARIATIONAL PRINCIPLES

Variational calculus has proved to be a convenient technique for solving problems governed by the linear diffusion law (Suo 1996, Pan *et al.* 1997, Cocks *et al.* 1999). Here we develop a virtual-power principle and a variational principle for the nonlinear diffusion problem. Only grain-boundary and free-surface diffusions are considered, since volume diffusion is almost irrelevant to nanosized particles. For the solid-state diffusion problem, the virtual-power principle can be expressed as the energy balance over a virtual variation δV in the atomic drifting velocity in the following format:

$$\sum_{\text{all atoms}} F \delta V \left(\frac{h dA}{\Omega} \right) + \sum_{\text{openings}} \mu \delta J (h d\Gamma) + \delta \left(\frac{dE}{dt} \right) = 0. \quad (15)$$

The first term in equation (15) is the virtual power of the driving force F which can be rewritten as

$$\sum_{\text{all atoms}} F \delta V \left(\frac{h dA}{\Omega} \right) = \int_{\text{GB+FS}} \frac{1}{\Omega} F \delta (hV) dA = \int_{\text{GB+FS}} \frac{1}{\Omega} F \delta j_h dA, \quad (16)$$

in which dA is a small element of the interface (grain boundary or free surface), GB represents grain boundaries, FS represents the free surfaces, h is the thickness of the diffusion layer, and $j_h = hV = h\Omega J$, which is a more convenient definition of the diffusive flux for grain-boundary and surface diffusions (volume of matter moving along the diffusion layer per unit time). The second term in equation (15) is included here for open systems and represents the virtual energy change due to atoms coming into or moving out of the system. This term can be rewritten as

$$\sum_{\text{openings}} \mu \delta J (h d\Gamma) = \int_{\Gamma} \frac{1}{\Omega} \mu \delta (h\Omega J) d\Gamma = \int_{\Gamma} \frac{1}{\Omega} \mu \delta j_h d\Gamma, \quad (17)$$

where Γ represents the opening parts of the system. The third term in equation (15) is the virtual change of the total free-energy rate of the system. We can write

$$E = \int_{\text{GB}} \gamma_{\text{gb}} dA + \int_{\text{FS}} \gamma_{\text{s}} dA, \quad (18)$$

where γ_{gb} and γ_{s} represent the specific energies for a grain boundary and the free surface respectively. From equation (7) we have

$$F = \frac{2kT}{a} \operatorname{arcsinh} \left(\frac{a}{2Dh} j_h \right). \quad (19)$$

Substituting equations (16)–(19) into equation (15) results in the following final version of the virtual-power principle:

$$\int_{\text{GB+FS}} \frac{2kT}{a\Omega} \operatorname{arcsinh} \left(\frac{a}{2Dh} j_h \right) (\delta j_h) dA + \int_{\Gamma} \frac{1}{\Omega} \mu \delta j_h d\Gamma + \delta \left(\frac{dE}{dt} \right) = 0, \quad (20)$$

which can be rewritten as

$$\delta \Pi = 0, \quad (21)$$

where Π is given by

$$\begin{aligned} \Pi = & \frac{2kT}{a\Omega} \int_{\text{GB+FS}} \left\{ j_h \operatorname{arcsinh} \left(\frac{a}{2Dh} j_h \right) - \left[\left(\frac{2Dh}{a} \right)^2 + j_h^2 \right]^{1/2} \right\} dA \\ & + \int_{\text{openings}} \frac{1}{\Omega} \mu j_h d\Gamma + \frac{dE}{dt}. \end{aligned} \quad (22)$$

Equations (21) and (22) provide a variational principle for solving the solid-state diffusion problem.

§ 5. A NONLINEAR SOLUTION FOR COBLE'S SINTERING PROBLEM

Coble (1970) solved the sintering problem using the linear kinetic law and provided an expression for the shrinkage of the two particles as a function of time. Coblenz *et al.* corrected an error in Coble's original expression which was later confirmed by Bouvard and McMeeking (1996) using numerical simulations. The correct expression is given by (Bouvard and McMeeking 1996)

$$\left(\frac{y}{R} \right)^3 = 3 \frac{\gamma_{\text{s}} Dh \Omega}{kTR^4} t. \quad (23)$$

Here the same problem is solved using the present nonlinear diffusion law. For the circular contact neck (grain boundary), mass conservation provides a relationship between the grain-boundary diffusion flux j_{gb} and the separation velocity V_{gb} between the two particles:

$$j_{\text{gb}} = -\frac{V_{\text{gb}} r}{2}, \quad (24)$$

where r is the coordinate from the centre of the neck. For the two-particle system, the free-energy rate can be written as

$$\frac{dE}{dt} = (2\pi c\gamma_s \sin \Psi)V_{gb}, \quad (25)$$

where Ψ is the dihedral angle. Coble (1970) considered only grain-boundary diffusion which is equivalent to treating the grain boundary as an open system. The boundary condition for the chemical potential μ at the edge of the contact neck is given by equation (13). Substituting equations (13), (24) and equation (25) into equation (20) yields

$$-\frac{2kT}{a\Omega} \int_0^c r^2 \operatorname{arcsinh} \left(-\frac{aV_{gb}}{4Dh} r \right) dr + c^2\gamma_s\kappa + 2c\gamma_s \sin \Psi = 0. \quad (26)$$

For a known value of the neck radius c , equation (26) is a nonlinear equation in terms of V_{gb} which can be solved using the Newton–Raphson method. From equation (12) we obtain

$$\frac{dy}{dt} = \frac{c}{2R} \frac{dc}{dt} = -\frac{1}{2} V_{gb}. \quad (27)$$

Equations (26) and (27) are numerically integrated using the direct Euler method to provide time evolutions for the neck radius c and the shrinkage y .

Figures 2(a)–(d) show the comparison between the nonlinear and the linear solutions for y/R as functions of time for four different particle radii. The material data used in the comparison are $a = 0.5$ nm, $\gamma_s = 1$ J m⁻², $\gamma_{gb} = \gamma_s/3$, $\Omega = 0.02$ nm³ and $T = 1160$ K. The time shown in the figure is normalized such that $\bar{t} = tDh$. Because of the log–log scale used for these figures, the linear solution given by equation (23) appears as straight lines for each of the cases, while the nonlinear solutions appear on the top of each of the straight lines. All the cases terminate at a common value of $y/R = 0.15$ which corresponds to a c/R value of 0.8. It can be seen from the figures that the nonlinear solution agrees with the linear solution for large particles ($R = 1000$ nm, for example), especially at the later stage of

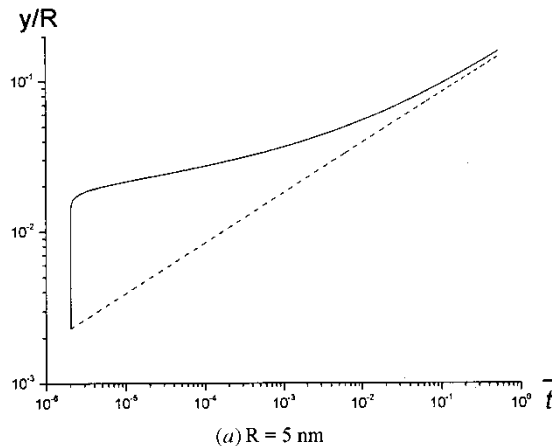


Figure 2. Comparison between the linear solution (---) and the nonlinear solutions (—) for the shrinkage between two spherical particles as functions of time.

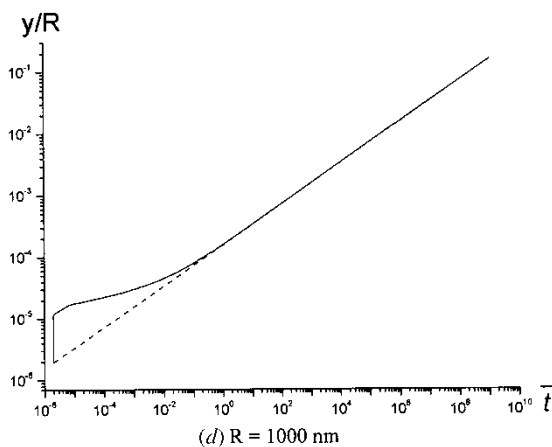
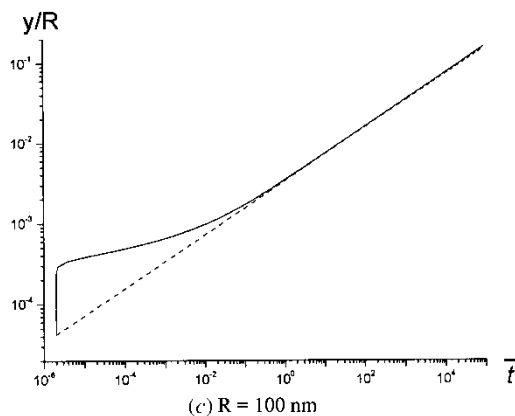
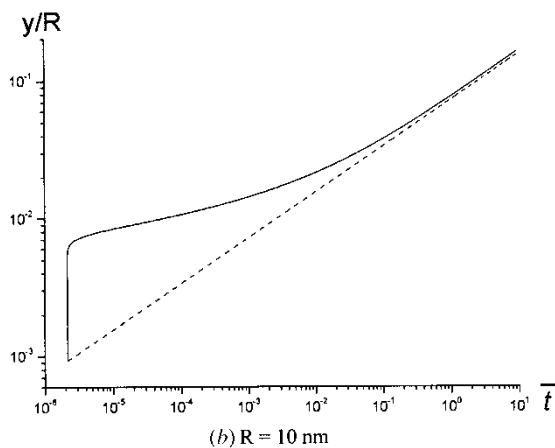


Figure 2. Continued.

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sintering where the driving force becomes smaller. For nanosized particles however, the linear diffusion law significantly underpredicts the sintering rate.

In general, surface diffusion may become as important as grain-boundary diffusion. The virtual-power principle or the variational principle developed in the present study can be used to construct finite-element schemes similar to those for the linear problems (Pan *et al.* 1997). A full numerical solution can then be obtained for microstructure evolutions in which the thermodynamic driving force is large and both surface diffusion and grain-boundary diffusion control the evolution.

REFERENCES

- BOUVARD, D., and McMEEKING, R. M., 1996, *J. Am. Ceram. Soc.*, **79**, 666.
 CAMPBELL, C. T., PARKER, S. C., and STARR, D. E., 2002, *Science*, **298**, 811.
 COBLE, R. L., 1970, *J. appl. Phys.*, **41**, 4698.
 COBLENZ, W. S., DYNYS, J. M., CANNON, R. M., and COBLE, R. L., 1980, *Proceedings of the Fifth International Conference on Sintering and Related Phenomena*, ed. by G. C. Kuczynski (New York: Plenum Press).
 COCKS, A. C. F., GILL, S. P. A., and PAN, J., 1999, *Adv. Appl. Mech.*, **36**, 81.
 HAGUE, D. C., and MAYO, M. J., 1995, *Mater. Sci. Engng*, **A204**, 83.
 JOHNSON, D. L., 1969, *J. appl. Phys.*, **40**, 192.
 PAN, J., 2003, *Intl. Mat. Rev.*, **48**, 69.
 PAN, J., COCKS, A. C. F., and KUCHERENKO, S., 1997, *Proc. R. Soc. A*, **453**, 2161.
 PAN, J., LE, H., KUCHERENKO, S., and YEOMANS, J. A., 1998, *Acta mater.*, **46**, 4671.
 SHEWMON, P. G., 1963, *Diffusion in Solids* (New York: McGraw-Hill).
 SUO, Z., 1996, *Adv. Appl. Mech.*, **33**, 193.
 TU, K. N., MAYER, J. W., and FELDMAN, L. C., 1992, *Electronic Thin Film Science* (London: Macmillan).