Coalescence of Spheres by Surface Diffusion

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The shape evolution of small heated metal particles is dominated by surface diffusion. When two spheres touch, they will thus merge into one, as they continually decrease their surface area. Focusing on the asymptotic behavior when the radius r of the neck joining the two spheres is still small, it is found that the metal does not stay simply connected, but encloses an intricate succession of toroidal voids. The temporal evolution of r exhibits a new type of self-similar behavior resulting from a discrete sequence of secondary singularities. [S0031-9007(98)05587-2]

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Powders of metal spheres are commonly merged into one continuous piece by heating, in a process called sintering. It is thus a fundamental problem in metallurgy [1,2] to understand the most basic mechanism behind this process, which is the coalescence of just two spheres in mutual contact. This should give information about the time required for coalescence and, with a detailed description of the small-scale motion, should allow predictions about the microstructure of the resulting material.

Below the bulk melting temperature, and on scales smaller than 10 μm, the motion of atoms along the surface is the dominant mechanism for mass transport [3]. Mullins and co-workers [3–5] derived the corresponding equations of motion for the surface shapes and investigated their properties in a series of papers. However, the singular shape of the initial profile makes the coalescence problem a very difficult one, both theoretically and numerically, and an asymptotic description of the resulting motion has remained an open problem.

Since large values of the surface curvature are concentrated around a very small region where the two spheres touch, one expects a very rapid local motion of the bridge joining the spheres. Thus, by analogy with similar fluid mechanics problems exhibiting singular behavior [6], the minimum radius r should exhibit power law scaling as a function of time. Below, we will see that, while power law behavior is indeed found, it is interrupted by a discrete sequence of secondary singularities, not unlike successive breakups driving a propagating front [7], which makes this problem quite different from previously known examples of power law scaling.

Qualitatively, motion by surface diffusion is not unlike the corresponding fluid mechanics problem of flow driven by surface tension, partly because the equilibrium states are the same. For example, a cylinder is prone to the surface-tension-driven Rayleigh-Plateau instability, which causes the cylinder to break up into a series of spheres, and so reduces the surface area. If these spheres meet, then for both surface-diffusion-dominated and fluid motion they will merge into one. However, the asymptotic description of the coalescence process is entirely different whether one is looking at the flow problem [8] or at surface diffusion, which is described below.

Figure 1 shows a schematic of two merging spheres of initial radius R and R/δ, where the local radius $h(z)$ of the figure depends on the position z along the axis of symmetry. Conservation of mass demands that

$$\partial_t h^2 + 2\partial_z(Jh) = 0\,, \tag{1}$$

where $J(z)$ is the projection of the surface mass flux onto the axis. This flux must be proportional to the gradient of the curvature, and thus

$$J = -\frac{B}{2}\,(\partial_z \kappa)/[1 + (\partial_z h)^2]^{1/2}, \tag{2}$$

with

$$\kappa = 1/(h[1 + (\partial_z h)^2]^{1/2}) - (\partial_{zz} h)/[1 + (\partial_z h)^2]^{3/2} \tag{3}$$

the curvature of a body of revolution. The additional factor of $1/[1 + (\partial_z h)^2]^{1/2}$ in (2) accounts for the fact that atoms travel parallel to the surface, while J is the flux in the z direction.

The fourth-order diffusion constant B has dimensions $\mathrm{cm}^4/\mathrm{sec}$, and thus a typical time scale for the merging is $\tau_R = R^4/B$. A typical value of B for a metal near the melting point is $B = 10^{-18}$ $\mathrm{cm}^4/\mathrm{sec}$ [3], and surface diffusion will dominate over volume diffusion on scales below 10 μm. In all of the following, we will use R and τ_R as units of length and time, respectively.

Sintering by surface diffusion was first considered by Kuczynski [1], who determined the coefficient of surface

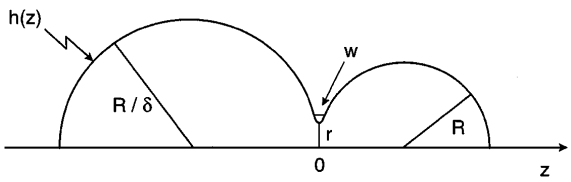

FIG. 1. The surface profile $h(z)$ produced by two coalescing drops of radius R and R/δ. The origin of the axis of symmetry $z = 0$ lies at the initial point of contact. The bridge joining the two spheres has a radius r and a width w.

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diffusion of various metals. It is instructive to repeat his arguments for deriving the time dependence $r(t)$ for small bridge radii r. Since the initial spherical shape near the point of contact has $h(z) \approx (2z)^{1/2}$, the width of the narrow gap between the spheres is $w \approx (r^2/2)(1 + \delta)$ (see Fig. 1), and thus the curvature $\kappa \approx r^{-2}$ in that region. To simplify the formulas, we will assume $\delta = 1$ below (equal spheres), but the arguments apply equally well to unequal spheres up to a simple geometrical constant. Assuming that the transition to $\kappa = O(1)$ occurs on the same scale w, the gradient of curvature is estimated to be w^{-2}, and the mass flux into the end of the gap is r/w^2. A mass $dm \approx rwdr$ is needed to increase the radius by dr, and by equating the flux with the change in mass we arrive at $\partial_t r \approx r^{-6}$. Integrating this equation, we find

$$r = (At)^{1/7}, \tag{4}$$

where $t = 0$ is the time when the spheres initially touched. The constant A remains to be determined.

Kuczynski [1] found good agreement between (4) and his experiments, but later numerical simulations [5] with initial radii as small as $r_0 = 0.05$ gave an exponent closer to $1/6$. It was thus concluded in [5] that the order of magnitude estimate leading to (4) needed improvement. To test the scaling theory in greater detail, we conducted simulations of (1)–(3) with $r_0 = 10^{-4}$, the results of which are shown in Fig. 2. We used a variant of a fully implicit finite difference code [9], developed earlier to describe the surface-tension-driven breakup of liquid threads. A nonuniform grid is chosen to ensure full resolution of the smallest scales, which are of the size 10^{-8}.

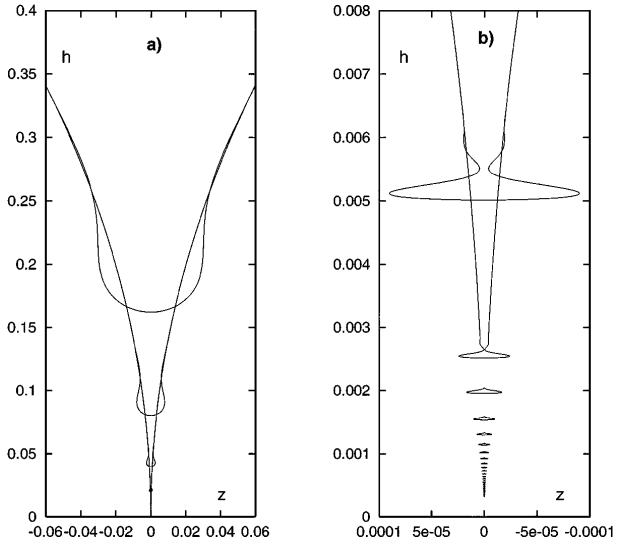

FIG. 2. Closeup views of the gap between two coalescing spheres of radius 1. Between two successive profiles shown in (a) the minimum radius r increases by a factor of 2. The top four profiles (going backwards in time) correspond to $\log_{10}(t) = -5.8$, -7.7, -9.4, and -11.2, respectively. (b) A further enlargement, with the sequence of voids visible at the bottom. Here the top four profiles were taken at $\log_{10}(t) = -17.5$, -18.3, -18.9, and -19.3. The voids are shown having the shapes they had upon enclosure.

The sequence of Fig. 2(a) shows a profile whenever r has increased by a factor of 2. One observes that the gap between the spheres is gradually filled in. However, for smaller r there is a pronounced hollow part at the end of the gap, which causes the profile to turn over, and after which $h(z)$ cannot be represented as a one-to-one function, so we transformed (1)–(3) to a representation $z(h)$, which always works in the region of interest. For small r, the width of the hollowed end continues to grow relative to the width of the gap, which contradicts the assumptions of Kuczynski's estimates, making the radius of curvature at the end larger than r^2. This result is even more apparent in the blowup of the small-r region of the same simulation shown in Fig. 2(b). At $r \approx 0.005$ the width of the hollow region is several times the gap width $w \approx r^2$. At the same time, the bulge above the hollow end has grown so much that the walls of the spheres almost touch, which eventually happens at $r \approx 0.002$, so that a toroidal void is enclosed inside the material. After this secondary singularity, the inner and outer surfaces evolve separately. Note the difference in scale between the axes, so contrary to its appearance the elliptical void is actually longer than it is wide.

To study the evolution further, whenever a void was enclosed we smoothed the tip of the outer channel on a scale r^2, and continued the simulation. From Fig. 2(b) it is apparent that an intricate succession of voids is produced when starting from a small initial radius, making the material highly porous. Only for $r \gtrsim 0.002$ does the tip of the channel recede sufficiently fast to escape further enclosure of air.

To understand the local dynamics near the tip in more detail, it is useful to look at the evolution on the scale of the gap width w. On that scale, the gap width remains almost constant, and since moreover $r \gg w$, the radius of curvature r can be neglected. The local dynamics are thus equivalent to the evolution of a straight channel carved out of a two-dimensional piece of material (see Fig. 3). Thus to study the local motion near the tip we consider the simplified initial condition of a semi-infinite channel of width one, using the same equations of motion as before. To be consistent with Fig. 2, we denote the distance from the initial tip of the channel by h. As the channel fills in, it is hollowed out to a much greater width than it had originally. This response occurs because the shape near the tip is nearly singular, represented by a large negative curvature, as seen in the right-hand part of Fig. 3, so that material cannot be replenished sufficiently fast through the channel, and has to come from the immediate neighborhood of the tip. This in turn leads to a region of positive curvature, which causes some material to flow back out of the channel. As a result, there is a pileup of material behind the hollow, which after a finite time grows large enough to touch down. Mathematically, this

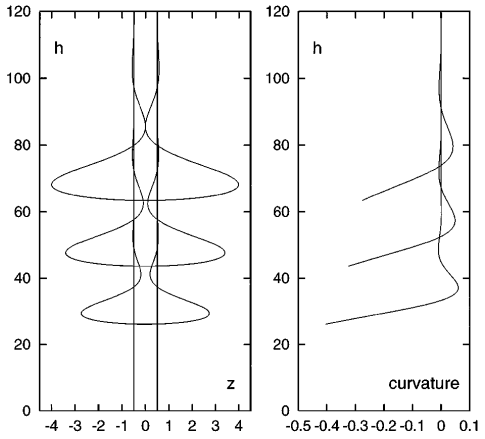

FIG. 3. Evolution of a semi-infinite straight channel of width 1, cut from a two-dimensional piece of material. At the left, the profile is shown; to the right, one can see the local curvature. While the groove fills in, it develops an increasingly pronounced hollow part at its end. Above the hollow part a bulge develops, which at time $\tau_0 = 7.4 \times 10^3$ closes off the gap. The preceding two profiles correspond to $\tau_0 = 3.2 \times 10^3$ and 1×10^3.

possibility comes from the oscillatory character of the Green function of the fourth-order diffusion equation [4]. The touchdown happens after a time $\tau_0 = 7.4 \times 10^3$, and at a distance $a = 85.5$ from the original tip. These numbers were determined from the simulation shown in Fig. 3. From dimensional analysis, the singularity time of a gap of width w is thus $\tau = w^4\tau_0$.

Applying this result to the original problem, the touchdown singularity will occur after a time $\tau = r_0^8\tau_0$, when starting from an initial radius r_0. On the other hand from (4) it is clear that the tip of the gap retracts only on a time scale $\tau_r = r_0^7/A$, which is slower. Thus, as long as

$$r_0 \lesssim r_{\text{void}} = 1/(\tau_0 A)\,, \tag{5}$$

voids will be enclosed continually, as seen in Fig. 2(b). To understand the asymptotics as $r_0 \to 0$, we therefore have to study the discrete steps of the forming voids, which can be obtained with a simple model. If the radius of the bridge is r_i at the last enclosure, it will be

$$r_{i+1} = r_i + aw_i = r_i + ar_i^2 \tag{6}$$

at the next, because the channel closes after the tip has receded a distance aw according to the simulation of Fig. 3. The total time elapsed since the first step is

$$t_i = \tau_0 \sum_{n=0}^{i} r_n^8 \tag{7}$$

according to the above estimates. While (6) and (7) are difficult to solve in closed form, the incremental change from one iteration is very small when r_i is small. Thus one can write (6) and (7) as a continuous evolution, which easily leads to

$$r = [7at/\tau_0 + r_0^7]^{1/7}. \tag{8}$$

Remarkably, for $r_0 = 0$, one thus recovers Kuczynski's law (4), which was based on the assumption of a continuous evolution beginning with $r(0) = 0$. Thus his estimates are still valid on the average, even if voids are being formed. Figure 4 shows the comparison of (8) with the numerical simulation of (1) and (2), using an initial radius of $r_0 = 10^{-4}$. Since the parameters a, τ_0 are taken from previous estimates, there is no adjustable parameter in the comparison. The excellent agreement starts to break down only at larger values of r, when the incremental change in r is no longer small. By comparing (8) and (4), the amplitude A from (4) can be identified as $A = 7a/\tau_0$, and thus voids are found below $r_{\text{void}} \approx 0.0017$ according to (5). Looking back at Fig. 2(b), this result is in good agreement with simulations. As pointed out before, for $r > r_{\text{void}}$ the width of the hollow shrinks faster than expected from the estimate $w \approx r^2$, leading to the larger exponent $1/6$ for $r(t)$, which is what was found by Nichols and Mullins [5]. The existence of this transient regime is again a consequence of the tendency of the dynamics to "undercut" a narrow passage.

So far we have not discussed the evolution of the voids after they have formed. To minimize surface area, their cross section will evolve to a circle. But the resulting torus in fact resembles a long, thin cylinder, which will then be unstable due to the surface diffusion analog of the Rayleigh-Plateau instability, forming a necklace of spherical voids. Note that this final instability breaks the rotational symmetry we have used throughout. Another

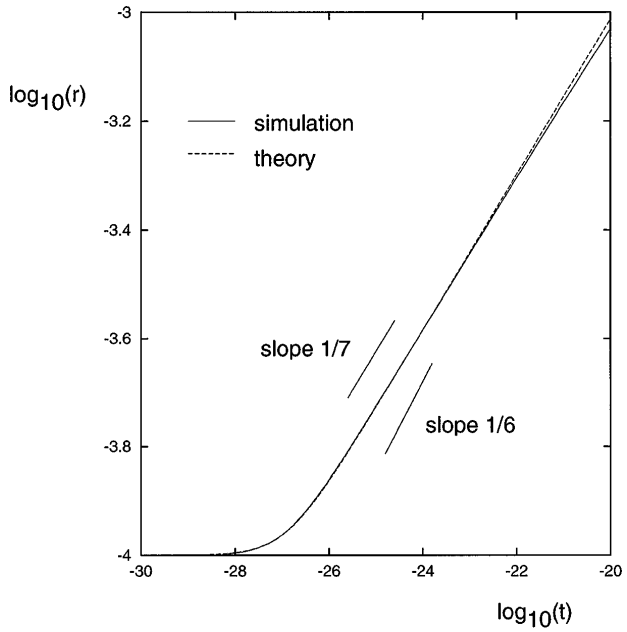

FIG. 4. A test of the scaling law (8) for the minimum radius as a function of time. The full line is the simulation, and the dashed line is the theoretical prediction. The initial radius is $r_0 = 10^{-4}$. The slope is very close to $1/7$, as predicted by our theory, while it differs noticeably from the transient slope of $1/6$, found by Nichols and Mullins [5].

detail of the subsequent evolution to be pointed out is the dynamics close to the point where the walls touch and close off a void. Asymptotically, this is the same as the problem of two spheres touching, but having much smaller initial radii. Thus for the formation of each void, the whole sequence of events is embedded here, in a process that repeats itself *ad infinitum*. Very soon of course the structures become so small that they are virtually impossible to follow even numerically.

Finally, it should be noted that the diameter of the largest spherical void is only 0.1 μm if the initial sphere radius is 1 mm. Above the roughening temperature [10], macroscopic facets disappear, and the surface is smooth down to atomic scales. By using one sphere as the tip of a scanning tunneling microscope, one should be able to make the approach of the two spheres in a very controlled fashion, such that contact is made on a nanometer scale [11,12]. Voids formed in the process of touching should therefore be confined to atomic scales as well. Thus allowing for a careful preparation of the two crystals, voids of the predicted size should be observable experimentally.

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