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STEFAN PROBLEMS FOR MELTING NANOSCALED PARTICLES

JULIAN M. BACK

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Stefan problems are moving boundary problems that model how pure materials undergo phase transitions due to the conduction of heat and exchange of latent heat energy. Their solution involves satisfying the heat equation in each phase (liquid and/or solid, say), subject to specific boundary conditions on the moving phase interface. As the location of the moving boundary is unknown in advance, Stefan problems are nonlinear. Despite appearing relatively simple, the solutions can display highly complicated behaviour leading to many theoretical studies, but also give accurate results for a wide range of industrial applications in physics and engineering.

McCue *et al.* [10] study a particular two-phase Stefan problem for a melting nano-sized particle. Their model includes the Gibbs–Thomson equation: a nanoscale condition where the melting temperature is dependent on the particle size, and includes surface tension effects (see also [5, 14]). They find that the inner solid core becomes superheated in the sense that the temperature of the solid is everywhere greater than the *size-dependent* melting temperature (albeit less than the bulk melting temperature), and is quickly followed by finite-time blow-up of the solution. An infinite temperature gradient develops at the moving boundary and the melting speed becomes unbounded. As with all types of finite-time blow-up, these predictions are unphysical, which is strange as the original problem without the Gibbs–Thomson effect is well posed. This mathematical blow-up suggests the model is incomplete.

In Chapter 3 (and [2]) we investigate two related moving boundary problems, both of which are particularly useful in demonstrating the key properties of a melting

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sphere with surface tension. The first is the ill-posed one-phase Stefan problem for a superheated solid in one Cartesian coordinate. This problem is known to exhibit finite-time blow-up, with behaviour reminiscent of that found in [10] for the two-phase Stefan problem for a melting sphere with surface tension. This unphysical behaviour is characterised by the speed of the moving boundary becoming unbounded and an infinite temperature gradient developing in the blow-up limit. A second one-phase problem simulates aspects of the spherical two-phase problem with surface tension. We study this novel moving boundary problem numerically. Our results support the hypothesis that the blow-up of the superheated Stefan problem and the more complicated two-phase Stefan problem for a melting sphere with surface tension are related, in that the two problems exhibit a similar type of finite-time blow-up.

The finite-time blow-up of the ill-posed one-dimensional Stefan problem for a supercooled liquid can be regularised by the addition of kinetic undercooling [7]. Kinetic undercooling provides a small correction term to the Gibbs–Thomson rule which, without the kinetic term, is derived under the assumption that the system is in equilibrium [8]. Equivalent moving boundary problems with kinetic undercooling are used to model the diffusion of solvents in glassy polymers [9, 12], or the flow of viscous fluid in a Hele-Shaw cell [4]. In Chapter 4 (and [1]), we consider the addition of kinetic undercooling to a particular energy conserving one-phase version of the full two-phase Stefan problem with surface tension for a melting sphere [13]. We use numerical simulation to show that kinetic undercooling regularises the finite-time blow-up of this problem, so that the model has solutions that remain regular right up to complete melting. The solutions also have rather interesting extinction behaviour, due to the competition between the surface tension and the kinetic undercooling.

Motivated by the results of Chapter 4, we consider the fully two-phase Stefan problem for a melting sphere with surface tension and kinetic undercooling in Chapter 5 (and [3]). We again consider the effects of kinetic undercooling on finite-time blow-up and show that the singular behaviour found in [10] is suppressed when kinetic undercooling is included. The results of this new model are found to be consistent with experimental findings of abrupt melting of nanoscaled particles. This problem is studied further in Chapter 6, where we examine the blow-up regime, regularisation by kinetic undercooling, and subsequent extinction behaviour more closely. To study the blow-up of the ill-posed problem, we consider a novel one-phase problem valid for times near blow-up [11], which is the spherical version of the problem in Chapter 3.

In Chapters 3–6, the density is assumed to be constant throughout the phase change process. In Chapter 7, we relax this assumption and study the Stefan problem with surface tension and density change effects (see also [6]). Specifically, we study this problem in the context of a density change as a regularising mechanism. We produce numerical solutions to two Stefan problems used in the literature, before adding kinetic undercooling as a second regularising mechanism. The competition between these two regularising mechanisms is also explored.

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In Chapter 7 we also develop a Stefan problem that accounts for size-dependent latent heat effects. We find that while this addition does not regularise finite-time blow-up, the results highlight the need for a regularising mechanism in these melting nanoparticle models.

In summary, the key contributions to the literature are twofold. The first is the development of a continuum model for a melting metal nanoparticle that provides physically reasonable results. The melting of small nano-sized particles is nonstandard, as the solid becomes locally superheated such that heat flows *into* the moving boundary from both phases. This local superheating leads to ill-posed behaviour in the (locally) superheated solid, but can be regularised with the addition of kinetic undercooling. We also utilise a material-dependent scaling to examine the melting behaviour of metal particles to produce actual physical predictions. The second contribution is an investigation into the finite-time blow-up which arises in several ill-posed Stefan problems, and the relationship between these problems. Possible regularisation mechanisms are considered, such as kinetic undercooling, density change, and the novel addition of size-dependent latent heat of fusion.

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JULIAN M. BACK, Mathematical Sciences,
Queensland University of Technology,
Brisbane QLD 4000, Australia
e-mail: jvlianback@gmail.com

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