Applied Mathematical Modelling 61 (2018) 1–17

Contents lists available at ScienceDirect

Applied Mathematical Modelling

journal homepage: www.elsevier.com/locate/apm

Asymptotic analysis of the Guyer–Krumhansl–Stefan model for nanoscale solidification

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ARTICLE INFO

Article history:
Received 16 October 2017
Revised 14 February 2018
Accepted 19 March 2018
Available online 11 April 2018

Keywords:
Stefan problem
Guyer-Krumhansl equation
Nanoscale phase change
Asymptotic analysis

ABSTRACT

Nanoscale solidification is becoming increasingly relevant in applications involving ultrafast freezing processes and nanotechnology. However, thermal transport on the nanoscale is driven by infrequent collisions between thermal energy carriers known as phonons and is not well described by Fourier's law. In this paper, the role of non-Fourier heat conduction in nanoscale solidification is studied by coupling the Stefan condition to the Guyer–Krumhansl (GK) equation, which is an extension of Fourier's law, valid on the nanoscale, that includes memory and non-local effects. A systematic asymptotic analysis reveals that the solidification process can be decomposed into multiple time regimes, each characterised by a non-classical mode of thermal transport and unique solidification kinetics. For sufficiently large times, Fourier's law is recovered. The model is able to capture the change in the effective thermal conductivity of the solid during its growth, consistent with experimental observations. The results from this study provide key quantitative insights that can be used to control nanoscale solidification processes.

1. Introduction

Advances in the field of nanotechnology are improving the efficiency, functionality, and cost-effectiveness of modern devices. Nanowire-based solar cells, for instance, offer several advantages over traditional wafer-based and thin-film technologies [1]. Furthermore, the unique physical properties of carbon nanotubes have enabled the fabrication of new electrochemical biosensors [2]. Nanotechnology is also playing an increasing role in biology and medicine [3], where it finds applications in drug and gene delivery [4], protein detection [5], and tissue engineering [6]. A key issue surrounding the use of nanoelectronic devices [7], nano-enabled energy systems [8], and nanomedicine [9] is that of thermal management [10,11]. The ability to successfully manipulate heat can be vital to device performance [12] and a lack of thermal regulation can lead to melting and device failure [13]. Understanding nanoscale heat transfer and phase change is therefore crucial for current and future applications of nanotechnology.

At the nanoscale, heat transfer and phase change become markedly different from their macroscopic counterparts. This is partially attributed to the increased ratio of surface-to-bulk atoms, which can introduce a size dependence to key thermodynamic parameters such as melt temperature [14–16], latent heat [17–19], and surface energy [20]. Furthermore, the mean free path of thermal energy carriers, known as phonons, can be on the order of hundreds of nanometers in crystalline

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https://doi.org/10.1016/j.apm.2018.03.026
0307-904X/

solids at room temperature [11]. As a result, thermal transport on the nanoscale occurs as a ballistic process that is driven by infrequent collisions between phonons, in contrast to macroscopic thermal transport, which is a diffusive process driven by frequent collisions and gradients in the temperature. The ballistic nature of nanoscale heat transport can lead to substantial decreases in the effective thermal conductivity of nanomaterials, which has been experimentally confirmed [11,21,22] in samples with length scales up to 10 microns [23], far beyond the nano-regime.

Extensive research has been carried out to develop practical theories of heat transport and phase change that are valid at the nanoscale. The role of size-dependent parameters in nanoparticle [24–29] and nanowire [30,31] melting has been studied using Fourier-based models of heat conduction [32]. However, models that are derived from Fourier's law can only capture diffusive thermal transport and lead to an infinite speed of heat propagation, in clear contrast to the ballistic nature of nanoscale heat transport observed in experiments. Several approaches have been aimed at addressing this shortcoming [33]. Cattaneo [34] proposed that a temperature gradient can only induce a thermal flux after a finite amount of time has passed. An expansion of the governing equations about small relaxation times leads to the hyperbolic heat equation (HHE), or Maxwell–Cattaneo equation, which captures the wave-like propagation of heat associated with ballistic transport. Although the HHE correctly describes heat propagation with finite speed, the introduction of a relaxation time is somewhat ad-hoc and masks the underlying physics of nanoscale thermal transport. Guyer and Krumhansl [35,36] later derived from the linearised Boltzmann transport equation an extension to the HHE which includes non-local effects and explicitly incorporates the phonon mean free path into the governing equations. The Guyer–Krumhansl (GK) equation is particularly appealing from a theoretical point of view because it provides a link between kinetic and continuum models and is based on well-defined physical parameters. Moreover, the striking similarity between the GK and Navier–Stokes equations enables nanoscale heat transport to be conceptualised in terms of fluid mechanics and this analogy has been used to rationalise the reduced thermal conductivity of nanosystems in terms of phonon hydrodynamics [33,37,38].

Theoretical studies of nanoscale phase change that incorporate non-Fourier heat transport are predominantly based on the HHE and originally focused on mathematical issues [39–41] and the correct form of boundary conditions [42,43]. Solomon et al. [44] developed an enthalpy formulation of the hyperbolic Stefan problem and used numerical simulations to show that increasing the relaxation time can alter the solidification kinetics. Liu et al. [45] compared the parabolic (classical) and hyperbolic Stefan problems in the context of thermal spray particles and concluded that flux relaxation only influences the early stages of solidification, which agrees with the earlier work by Sadd and Didlake [46]. As shown by Mullis [47], hyperbolic heat transport can strongly influence the formation of dendrites in rapidly solidifying metal baths. Recently, the hyperbolic Stefan model has been applied to solidification problems arising in pulsed-laser surface treatment [48], cryopreservation of skin [49] and other biological tissues [50], and cryosurgery of lung cancer [51]. Sobolev [52] derived the GK equation from a two-temperature model and coupled it to the Stefan condition to study ultra-fast melting and solidification in the context of pulsed-laser experiments. This study, however, was restricted to the case of constant interface velocities and travelling-wave solutions for the temperature and flux.

In this paper, we carry out a detailed investigation of nanoscale solidification by coupling the GK equation to the Stefan condition. Matched asymptotic expansions are used to solve the free boundary problem without prior assumptions about the form of the solution and interface velocity. The systematic asymptotic analysis clearly elucidates the relationship between non-Fourier heat transport and the kinetics of solidification, and demonstrates the occurrence of large deviations from the classical behaviour predicted by Fourier's law. To the best of our knowledge, this is the first time that matched asymptotic expansions have been used to study non-Fourier Stefan problems.

The paper is organised as follows. In Section 2, a one-phase model for one-dimensional nanoscale solidification is presented. The model focuses on heat conduction through the solid as described by the GK equation. Asymptotic solutions to the one-phase model are computed in Section 3 and used to understand how non-Fourier heat transport affects the solidification process. The paper concludes in Section 4.

2. Model formulation

We consider the growth of a nanoscale solid into a semi-infinite liquid bath, as depicted in Fig. 1. We will assume that one side of the bath is exposed to a cold environment that is held at a temperature T_e that is below the freezing temperature T_f. The solidification process will, therefore, be solely driven by the transfer of heat from the bath into the environment. Newton's law will be used to model the exchange of thermal energy between the solid and surrounding environment. The

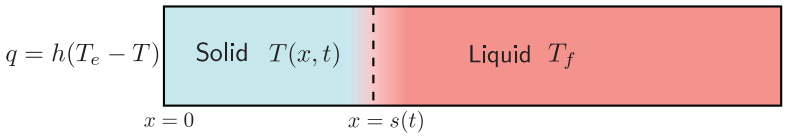

Fig. 1. The solidification of a semi-infinite liquid bath that is in contact with a cold environment with temperature T_e. The transfer of heat from bath into the environment drives the solidification process and is modelled using a Newton boundary condition with a heat transfer coefficient h. The position of the planar solid-liquid interface is denoted by $x = s(t)$.