2008

Mathematical modelling of nanoparticle melting or freezing

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A thesis submitted in fulfillment of the

requirements for the award of the degree of

Doctor of Philosophy

from

University of Wollongong

by

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2008

CERTIFICATION

I, Bisheng Wu, declare that this thesis, submitted in fulfilment of the requirements for the award of Doctor of Philosophy, in the School of Mathematics and Applied Statistics, University of Wollongong, is wholly my own work unless otherwise referenced or acknowledged. The document has not been submitted for qualifications at any other academic institution.

Bisheng Wu

May, 2008

Acknowledgements

First of all I would like to express my sincere gratitude to my principle supervisor, Professor James M. Hill, for his constant encouragement and guidance over the past three years. He has walked me through all the stages of the writing of this thesis and without his help this thesis could not have reached its present form.

Thanks are also due to my associate supervisors: Dr. Pei Tillman and Dr. Scott W. McCue, whose insightful comments and advice have been a source of inspiration.

Additionally, I'm very fortunate to be studying in the Nanomechanics Group at the University of Wollongong, which provides a good academic atmosphere. In the group there are excellent members who, living like a family, help each other in daily life. Moreover, the weekly impassioned talks and presentations benefit us greatly. It has become a rewarding experience and one that I will treasure all of my life.

Abstract

This thesis presents a mathematical modelling in nanotechnology. Many experiments and molecular dynamics simulations demonstrate that the melting point of nanoparticles shows a size-dependent characteristic in the nanoscale. Based on the assumption that the material is a pure one, the melting process of spherical and cylindrical particles, especially nanoparticles, is treated as a Stefan moving boundary problem. Analytical or semi-analytical approaches, such as small-time perturbation expansions with front-fixing techniques, large Stefan number limit, integral iterative scheme, and numerical methods, such as enthalpy scheme and front-fixing method, are applied to the one- and or two- phase Stefan problem in spherical and cylindrical domains by taking into account the effect of the interfacial or surface tension. The results from these methods are compared and show excellent agreement to some extent. This thesis may provide a possibility of explaining some interesting phenomena occurring in the physical experiments, i.e. superheating and "abrupt melting", or work as a guide for the potential applications of nanoparticles, for example, drug delivery, nanoimprinting and targeted ablation of tumor cells

In Chapter 1, a simply survey of the research background is given. Chapter 2 studies the full classical two-phase Stefan problems without surface or interfacial tension. By using the approach from large Stefan number limit and small-time perturbation methods, long- and short-time solutions are obtained, and the results from these methods are compared with the numerical enthalpy scheme. The limits of zero Stefan-number and slow diffusion in the inner core are also noted. Chapter 3 presents the melting of a spherical or cylindrical nanoparticle by including the effects of surface tension through the Gibbs-Thomson condition. A single-phase melting limit is derived from the general two-phase formulation, and the resulting equations are studied analytically in the limit of small time and large Stefan number. Further analytical approximations for the temperature distribution and the position of the solid-melt interface are found by applying an integral formulation together with an iterative scheme. All these analytical results are compared with numerical solutions obtained using a numerical front-fixing method, and they are shown to provide good approximations in various regimes. In Chapters 4 and 5, the methods used in above sections are extended to the melting problem for spherical and cylindrical

nanoparticles, respectively. The results from these approaches are compared with those from the numerical front-fixing method.

The original contributions of this thesis are: approximate analytical solutions are obtained for the classical two-phase Stefan problems in a spherical domain; a general single-phase limit for the melting of nanoparticles are derived and analyzed with the correct boundary conditions; a critical radius is found to exist for the blow-up of the one-phase melting; the melting process of spherical and cylindrical nanoparticles are studied analytically from the perspective of Stefan moving boundary problem by including the effect of surface tension; some interesting phenomena observed in physical experiments, i.e. superheating and "abrupt melting", are explained in terms of Stefan problems.

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Nomenclature

k_ℓ^*, k_s^* the thermal conductivities of the solid and liquid phases, respectively

$c_\ell{}^*$, c_s^* the specific heat of the solid and liquid phases, respectively

σ_{sv}, σ_{lv} the interfacial tension between the solid and vapor phases and between the liquid and vapor phases, respectively

T_ℓ^*, T_s^* the physical temperatures of the liquid and solid phases, respectively

T_ℓ, T_s the dimensionless temperatures of the liquid and solid phases, respectively

T_a^* the physical temperature of particle surface

V^*, V the physical and dimensionless initial temperatures of the particle

T_m^* the fusion temperature of the bulk material of the particle

R^*, R the physical and dimensionless positions of the solid/liquid interface

a^* the initial radius of the particle

$T_f^*(R^*)$ the equilibrium temperature at the solid/liquid interface

κ the ratio of the thermal conductivities k_s^*/k_ℓ^*

δ the ratio of the specific heat $c_s^*/c_\ell{}^*$

L the latent heat of fusion

λ the interfacial tension coefficient

α the Stefan number $\alpha = L/[c_\ell(T_a^* - T_m^*(1 - \omega/a^*))]$

β the effective Stefan number $\beta = \alpha - \sigma(1 - \delta) - \delta V$

σ the parameter related to the interfacial tension