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# Simulating the superheating of nanomaterials due to latent heat release in surface reconstruction

Amit Singh, E.B. Tadmor *

*Department of Aerospace Engineering and Mechanics, The University of Minnesota, Minneapolis, MN 55455, United States*

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ABSTRACT

Surface reconstruction and phase transformation in nanomaterials can result in a significant rise in temperature due to the release of stored energy called "latent heat." To simulate this behavior, we propose a hybrid continuum partial differential equation for non-Fourier heat transfer with a stochastic source term modeled using a kinetic Monte Carlo (KMC) algorithm for time-dependent rates to account for the latent heat release as the temperature is changing. The parameters required for the method are obtained through independent atomistic calculations. This includes energy barriers for KMC rates obtained using nudged elastic band calculations, and the non-Fourier thermal parameters obtained using a novel thermal parameter identification scheme described in this paper. As a demonstration of the approach, we study the superheating of silicon nanobeams observed in non-equilibrium molecular dynamics (NEMD) simulations. In these simulations, silicon (001) surfaces undergo a reconstruction from the ideal diamond crystalline surface to a reconstructed structure involving the formation of rows of dimers along a ⟨110⟩ direction. This reconstruction is accompanied by latent heat release that causes the nanobeam to dramatically superheat. The evolution of the nonuniform temperature profile along the nanobeam predicted by the continuum–KMC method is in excellent agreement with the NEMD results. A logarithmic dependence of the superheating temperature on nanobeam length is observed and theoretically discussed.



## 1. Introduction

Surface reconstruction and phase transformations in materials are often accompanied by the release of stored energy referred to as "latent heat." In nanomaterials, where the surface-to-volume ratio is high, this energy constitute a significant increase to the overall energy of the system and can therefore cause significant heating. A recent example is described by Zheng et al. [1] who observed superheating of $Cu_2S$ nanorods due to phase transformations from a low-chalcocite to a high-chalcocite phase induced by electron beam heating. Our objective in this paper is to discuss the phenomenon of superheating due to latent heat release and to develop a predictive simulation methodology for problems of this nature using parameters obtained separately by atomistic calculations.

As a motivating example, we focus on the relatively simple problem, observed in non-equilibrium molecular dynamics (NEMD) simulations that we performed, of superheating of silicon nanobeams terminated by {001} surfaces. The Si(001) surface is known to undergo a reconstruction that involves the formation of rows of dimers along ⟨110⟩ directions [2]. In the NEMD simulation, the nanobeam temperature is initially at 10 K and then the temperature of both ends is raised to 30 K and maintained at this level.[1] Fig. 1 shows a series of temperature profiles at increasing time. The interior of the beam gradually heats up, but rather than stabilizing at 30 K as expected, a dramatic overshooting in temperature that exceeds 200 K occurs due to release of latent heat that accompanies dimer formation in the reconstruction process. The maximum temperature is reached after 231 ps after which the temperature gradually decreases back to 30 K as the excess heat is absorbed at the ends. This is an interesting example that captures all of the main features of the superheating phenomenon in a well-studied system. We stress however that this is only an

* Corresponding author.
*E-mail address:* tadmor@umn.edu (E.B. Tadmor).

[1] Initially, periodic boundary conditions are applied in all directions to create a bulk during the equilibration stage at the initial temperature of $\theta_0 = 10$ K. Periodicity is then removed along the vertical direction of the beam so that the top (001) and bottom ($00\bar{1}$) surfaces are exposed. Periodicity is maintained along the other directions during the simulation, so that the "nanobeam" is really an infinite nanoslab with finite thickness. For this reason the side atoms on the (010) and ($0\bar{1}0$) surfaces do not reconstruct.

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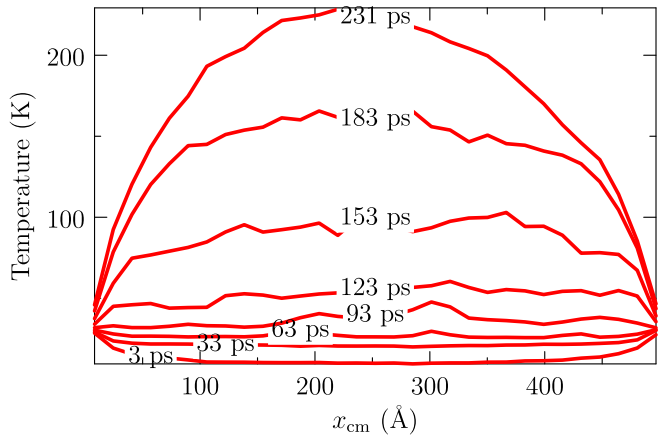


**Fig. 1.** NEMD temperature profiles at increasing time for a silicon nanobeam of size $505 \times 16.3 \times 16.3$ Åwith an initial temperature of 10 K and with the ends held at 30 K. Each profile is an average over 3 ps. The profiles are marked with their corresponding times.

academic example[2] since in experiments under vacuum conditions silicon surfaces reconstruct at temperatures as low as [3] 5 K.

To model the superheating phenomenon we propose a continuum partial differential equation (PDE) for non-Fourier heat transfer [4] parametrized using a novel thermal parameter identification (TPI) scheme based on an iteratively reweighted least squares (IRLS) regression method [5]. The injection of energy due to the latent heat released by dimerization is modeled using a stochastic Kinetic Monte Carlo (KMC) algorithm [6] that is coupled to the continuum PDE through the source term. A time-dependent KMC approach [7] is used since the temperature along the nanobeam, and hence the transition rates, are changing during the KMC process. The KMC rates are estimated using harmonic transition state theory (h-TST) with the activation barrier for dimer formation computed from the atomistic model using the climbing-image nudged elastic band (CI-NEB) method [8]. We find that the predictions of the hybrid continuum–KMC method for the silicon nanobeam example are in excellent agreement with the NEMD results. Using our model we are able to study larger systems than are readily accessible via NEMD. We find a logarithmic dependence of the superheating temperature on nanobeam length and provide a theoretical explanation for this observation.

The structure of the paper is as follows. In Section 2, we begin with a brief overview of Fourier and non-Fourier heat conduction models. In Section 3, we describe the TPI-IRLS procedure for extracting thermal parameters from the NEMD temperature profiles obtained prior to surface reconstruction. The results of applying TPI-IRLS to silicon are described in Section 4. In Section 5, the surface reconstruction on the Si(001) surface and activation barriers for dimerization are studied. In Section 6, we describe the hybrid continuum–KMC method that models the latent heat released during the surface reconstruction process and predicts the evolution of the temperature profiles. We conclude in Section 7 with a summary and suggestions for future work.

## 2. Fourier and non-Fourier heat transfer models

The simplest theory of heat conduction assumes Fourier's law. For a one-dimensional (1D) homogeneous body, this can be written as

$$q = -k(\theta)\frac{\partial \theta}{\partial x}, \tag{1}$$

where $q = q(x,t)$ and $\theta = \theta(x,t)$ are the heat flux and temperature, respectively, at position $x$ in the current configuration at time $t$, and $k(\theta)$ is the temperature-dependent thermal conductivity.

The energy equation for a rigid solid body without heat sources is (see for example Section 10.2 in [9])

$$\frac{\partial e}{\partial t} = \gamma \frac{\partial \theta}{\partial t} = -\frac{\partial q}{\partial x}, \tag{2}$$

where $e = e(x,t)$ is the internal energy per unit volume and $\gamma = \partial e/\partial \theta$ is the volumetric heat capacity. Substituting the expression for $q(x,t)$ in Eq. (1) into Eq. (2), we obtain Fourier's heat equation for a temperature-dependent thermal conductivity:

$$\gamma \frac{\partial \theta}{\partial t} = k'(\theta)\left(\frac{\partial \theta}{\partial x}\right)^2 + k(\theta)\frac{\partial^2 \theta}{\partial x^2}, \tag{3}$$

where $k' = dk/d\theta$. This is a parabolic PDE that describes heat transfer as a diffusive process and assumes infinite speed of heat propagation.

In order to account for wavelike heat propagation at finite speed, Cattaneo [10,11] and Vernotte [12,13] introduced a relaxation time $\tau_q$ into the heat flux constitutive relation in Eq. (1). This leads to a non-Fourier model for heat flux:

$$\tau_q \frac{\partial q}{\partial t} + q = -k(\theta)\frac{\partial \theta}{\partial x}. \tag{4}$$

Taking the derivative of Eq. (4) with respect to $x$ and substituting in the energy equation in Eq. (2), yields the Cattaneo-Vernotte (CV) wave equation,

$$\gamma \tau_q \frac{\partial^2 \theta}{\partial t^2} + \gamma \frac{\partial \theta}{\partial t} = k'(\theta)\left(\frac{\partial \theta}{\partial x}\right)^2 + k(\theta)\frac{\partial^2 \theta}{\partial x^2}. \tag{5}$$

An alternative non-Fourier model for heat transfer was proposed by Joseph and Preziosi [4] based on earlier work by Gurtin and Pipkin [14] and Nunziato [15]. They refer to their model as a "Jeffreys-type" heat flux constitutive relation due to an analogy with a stress model developed by Jeffreys [16]. The Jeffreys-type model has the form [17]:

$$\tau_q \frac{\partial q}{\partial t} + q = -k(\theta)\frac{\partial \theta}{\partial x} - \tau_\theta k(\theta)\frac{\partial^2 \theta}{\partial x \partial t}, \tag{6}$$

where $\tau_\theta$ is an additional relaxation time. Following the procedure outlined above leads to a Jeffreys-type equation for the temperature:

$$\gamma \tau_q \frac{\partial^2 \theta}{\partial t^2} + \gamma \frac{\partial \theta}{\partial t} = k'(\theta)\left(\frac{\partial \theta}{\partial x}\right)^2 + k(\theta)\frac{\partial^2 \theta}{\partial x^2} + \tau_\theta \left[k'(\theta)\frac{\partial \theta}{\partial x}\frac{\partial^2 \theta}{\partial x \partial t} + k(\theta)\frac{\partial^3 \theta}{\partial x^2 \partial t}\right]. \tag{7}$$

Assuming the following phenomenological relation for the thermal conductivity,

$$k(\theta) = k_0(\theta/\theta_0)^s, \tag{8}$$

where $k_0$ is the thermal conductivity at temperature $\theta_0$, and $s$ is a real exponent, the Jeffreys-type equation can be written as

$$\frac{\partial \theta}{\partial t} = -\tau_q \frac{\partial^2 \theta}{\partial t^2} + \frac{k_0}{\gamma}\left[\left(\frac{\theta}{\theta_0}\right)^s \left(\frac{s}{\theta}\left(\frac{\partial \theta}{\partial x}\right)^2 + \frac{\partial^2 \theta}{\partial x^2}\right)\right] + \frac{k_0 \tau_\theta}{\gamma}\left[\left(\frac{\theta}{\theta_0}\right)^s \left(\frac{s}{\theta}\frac{\partial \theta}{\partial x}\frac{\partial^2 \theta}{\partial x \partial t} + \frac{\partial^3 \theta}{\partial x^2 \partial t}\right)\right]. \tag{9}$$

The CV wave equation and the Fourier equation follow from this equation as special cases with $\tau_\theta = 0$ and $\tau_q = \tau_\theta = 0$, respectively.

[2] Since the focus of the paper is on the simulation methodology, with the silicon nanobeam problem serving as an example, we do not pursue quantum corrections that would improve the accuracy of predictions at low temperatures.