

SURFACE KINETICS OF NANOCCLUSERS

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Abstract. Surfaces are responsible for many unique features exhibited by the nanoclusters. Even though numerous theoretical and experimental studies have been done to understand the nature of free surfaces, much emphasis has not been put on understanding the dynamics of free boundaries at the fundamental atomistic scale of length and time. In the present work we use the techniques of molecular dynamics to filter out the dynamics of the boundaries from that of the entire nanocluster. We show that at a given thermodynamic temperature, the effective statistical temperature is different for the free boundaries. Despite this observation, the surface dynamics seems to be in strong correlation with the rest of the system. This uniqueness of the surface in terms of its kinetics is expected to be crucial in the phenomena of melting and mechanochemical synthesis.

1. INTRODUCTION

The behavior of nanoclusters in general, is often governed by the behavior of their surfaces on account of a large surface to volume ratio. The surfaces typically have dangling bonds, which manifests in a range of interesting features. Out of all the effects, the influence of free surface on the thermodynamics and kinetics of nanoclusters at finite temperatures remain the most controversial. For instance, the lowering of melting point of a nanocluster is explained in several ways: one of the theories takes into account the reduction in the per atom cohesive energy and its outcome in terms of the Lindemann's criterion [1,2]; the other theories deal with the liquid drop model [3], the liquid shell nucleation model [4,5] and the liquid nucleation and the growth model [6] etc. However, amid multiple proposed ideas, the most widely accepted view is that the melting initiates at the surface of the nanocluster long before the bulk melting temperature is attained. Premelting of nanoclusters can also be considered in the same context.

Similarly, the kinetics of surface is expected to play a significant role in the mechanochemical synthesis of nanomaterials. Several mechanisms of this process have been proposed in the theoretical perspective [7]. In one of them, the mechanochemical activation of the precursor is the most vital stage. It involves enhanced defect densities, smaller lengths of diffusion and large activated surfaces etc. On the other hand, the mechanism of activation assisted phase formation deals with the circumstances, where a direct synthesis does not occur. Instead, the temperature of phase formation is reduced significantly due to defects and small particle size. In the well known example of BaTiO₃, very high speed milling of the precursors BaO and TiO₂ produces the ferroelectric at room temperature, while comparatively lower milling rate is found to reduce the reaction temperature in calorimetric experiments [8]. Although there is an instantaneous rise in temperature due to impact, it is still lower than the normal reaction temperatures in such cases. Recently, Smolyakov and co-workers [9] have developed a

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macroscopic thermodynamic model of mechanochemical processing. Nevertheless, despite the fact that the surface of a nanoparticle exhibit a different response to elevated temperatures, the role of surface kinetics has not been explored comprehensively in this regard.

The present work is aimed at studying the fundamental dynamics of surface atoms at a given temperature. Unlike the earlier studies, instead of treating the system as the whole, we split it into the subsystems of its surface and the interior (which we shall refer as “core” in this paper). In order to emphasize that our treatment is a general one, we study the simple case of a 2-D square lattice and Lennard-Jones interatomic interaction with nearest neighbor bonding. We reveal that at finite temperatures, the boundary follows a dynamics quite different from the core, even in such a fundamental case study. Our conclusions reveal that this effect can play a significant role in governing the phenomenon of premelting and mechanochemical synthesis.

2. SIMULATION METHODOLOGY

Molecular dynamics (MD) simulation strategy has been employed for this purpose. We create $N \times N$ square lattice using the Lennard – Jones 12-6 potential.:

$$U(r) = 4\epsilon_0 \left[\left(\frac{\sigma_0}{r} \right)^{12} - \left(\frac{\sigma_0}{r} \right)^6 \right], \quad (1)$$

where r is the interatomic distance with equilibrium value $a = 2^{1/6}\sigma_0$, and ϵ_0 is the depth of the potential well. We assume nearest neighbor interactions, i.e. each atom is supposed to be connected to the adjacent four atoms through the interaction given in Eq. (1). For small displacements, the potential function can be approximated as a harmonic oscillator

with the effective spring constant $k = \left. \frac{\partial^2 U(r)}{\partial r^2} \right|_{r=a}$. In

this study we express the potential parameters in terms of a and k . Without any loss of generality, we assume arbitrary scaled units for the physical dimensions such that a and k have the numerical values 1 and 1×10^{-6} respectively, when the temperature is expressed in Kelvin with unity as the Boltzmann’s constant. All the simulations are done under the canonical (NVE) ensemble condition.

For the purpose of simulations, we assign initial random velocities such that the centre of mass has no net velocity. With this initialization, the Velocity-Verlet algorithm [10] is used to track the phase space evolution of the system as:

$$\mathbf{v} \left(t + \frac{\delta t}{2} \right) = \mathbf{v}(t) + \frac{1}{2} \mathbf{a}(t) \delta t$$

$$\mathbf{r}(t + \delta t) = \mathbf{r}(t) + \mathbf{v} \left(t + \frac{\delta t}{2} \right) \delta t,$$

$$\mathbf{a}(t + \delta t) = -\frac{1}{m} \nabla U(\mathbf{r}), \quad (2)$$

$$\mathbf{v}(t + \delta t) = \mathbf{v} \left(t + \frac{\delta t}{2} \right) + \frac{1}{2} \mathbf{a}(t + \delta t) \delta t.$$

Here the mass m of each atom is assumed to be unity. \mathbf{r} , \mathbf{v} and \mathbf{a} are the atomic coordinates, velocities and accelerations respectively. The time step is chosen to be $\delta t = (\pi/100) \sqrt{m/k}$. We define the instantaneous temperature as $T = \frac{m}{2N^2 k_B} \sum_i v_i^2$. Thermodynamically, this relation is appropriate for harmonic potential, still we adopt it to observe the effect of anharmonicity to make the study more general in nature.

3. RESULTS AND DISCUSSIONS

We initialize and rescale the velocities to start with initial temperatures of 800K, 1000K, 1200K, and 1400K. On account of the equipartition theorem, for perfectly harmonic potentials, the final temperatures must settle at half of the initial values, i.e. at 400K, 500K, 600K, and 700K respectively. This is due to equal sharing of the total energy between the potential and kinetic modes [11]. Here we vary the size N so that the effect of a varying surface/volume ratio can be observed. All the simulations are run for 10000 time steps during which the kinetic energy of every atoms is recorded. Later on, the in-

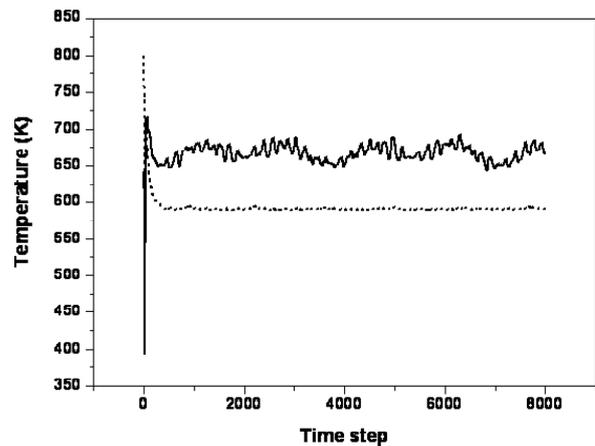


Fig. 1. Evolution of temperature with time step. The solid plot corresponds to the boundaries, whereas the dotted plot indicates the total temperature.

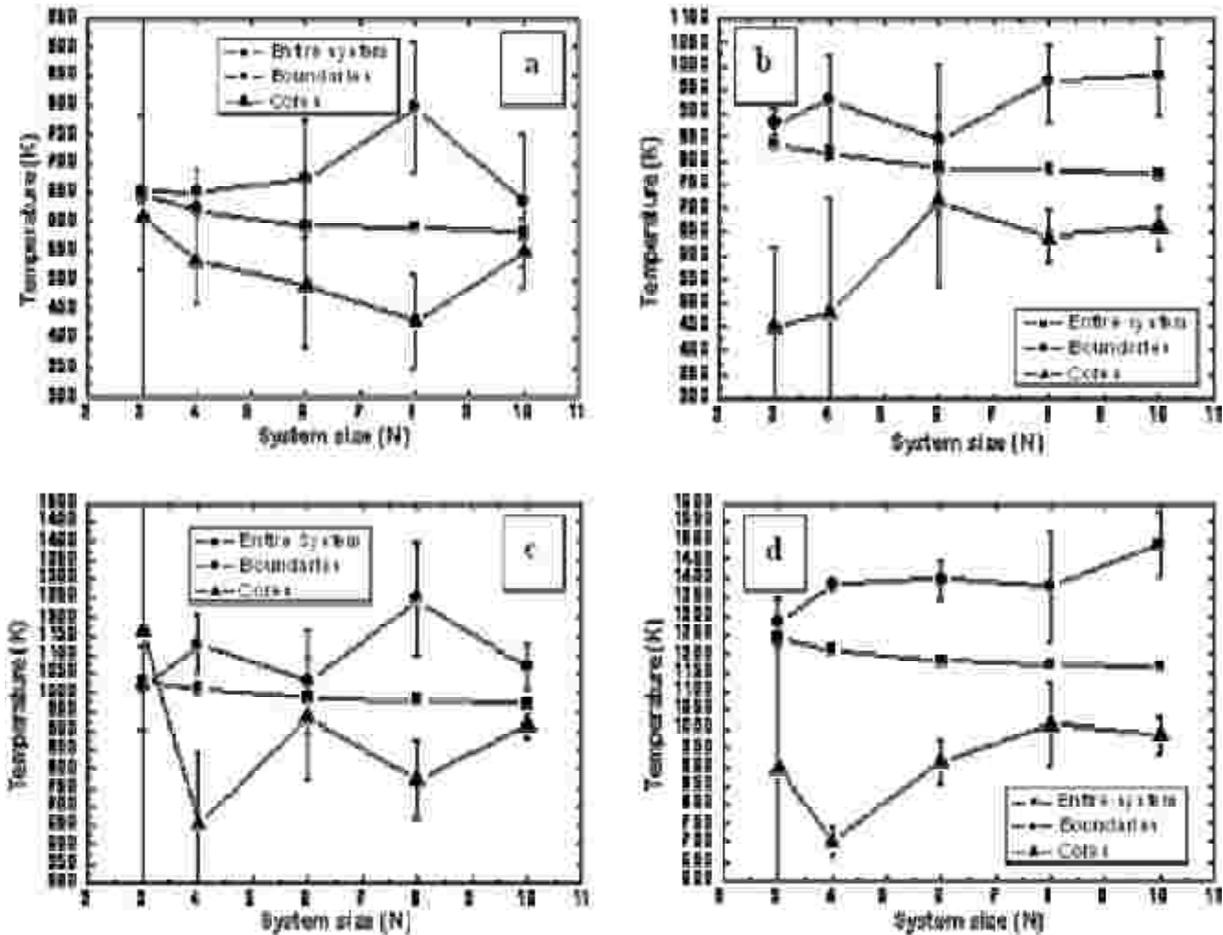


Fig. 2. System size vs. final temperatures for the initial temperatures of (a) 800K (b), 1000K, (c) 1200K, and (d) 1400K. The circular and triangular symbols show the boundary and core temperatures respectively. The square symbols show the overall temperatures of the systems. Error bars indicate the statistical fluctuations over several simulation runs.

stantaneous temperature of both the entire system and that of the atoms at the boundaries are calculated separately.

Fig. 1 shows a typical result for a simulation run at target temperature of 400K. One can observe that even though the initial temperature is 800K, the final temperature settles much above the ideal value of 400K. This is partly due to the finite size of the system, and partly due to the anharmonicity of the potential, which becomes more significant at large temperatures. Another astonishing observation is a higher final temperature for the boundary as compared to the overall temperature. It is clear from the figure, that we have yet not defined the term final temperature precisely as there are always some fluctuations in time. For the purpose of quantitative analysis, we note down the mean values of the last 4000 steps and refer to them as the final temperatures.

The mean values of the temperatures of the boundaries, cores and the entire systems are plotted in Fig. 2. We find that the total temperature of the system systematically reduces with increase in N . This corresponds to the above stated size-effect which disappears in a large enough system. Despite a reduced temperature at larger N , the system is still away from the ideal target temperature (half of the initial temperature) corresponding to the harmonic potential. This is attributable to the anharmonicity of the Lennard-Jones potential.

A different trend is observed for the boundary and core temperatures. In contrast to the trend of the total temperature of the system, there is no specific trend visible here. We see that the boundary temperature shows a general trend of exceeding that of the core. Moreover, another critical observation is the statistical fluctuation in the simulation outcomes. Both surface and core temperatures exhibit large

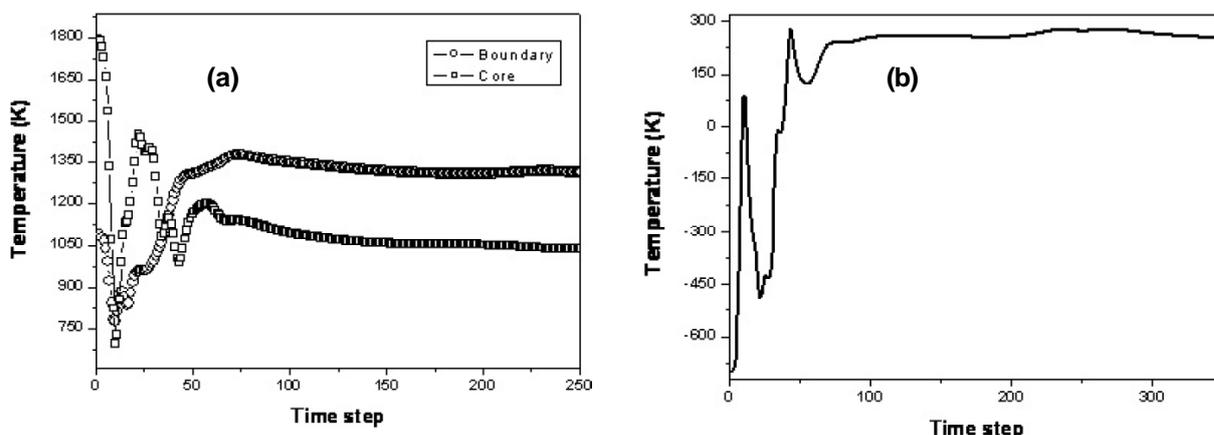


Fig. 3. (a) Initial stage of a typical simulation run. Despite its initial lower value, the boundary temperature ultimately exceeds the core temperature. (b) Exchange between the boundary and core temperatures.

statistical fluctuations as characterized by the corresponding error bars in Fig. 2. On the other hand, the total temperature of the system which comprises of both the core and the boundary shows a fluctuation that is negligibly smaller than that of its individual components. It indicates that the statistical temperature fluctuation of the surface is effectively coupled with that of the core by means of some thermal communication.

The strange results of these simulations can be attributable to the effective degrees of freedom of the system. The atoms at the boundaries are loosely bound and experience a different surrounding as compared to the other atoms. This manifests in a larger share of the boundary atoms in the total degrees of freedom of the system. On account of the equipartition theorem, the boundary therefore gets an asymmetric share of the net kinetic energy. As the temperature is an indicative of the average kinetic energy per atom, we observe a larger boundary temperature. This is a particularly special case where this circumstance arises in the equilibrated steady state. Thus, a constant temperature difference is maintained between the boundary and the interior without a net heat flow, even though the periphery and the interior are in direct physical contact. Fig. 3a shows the initial stage of a typical thermalization. Here we see that the initial random velocities are such that they give a much larger initial temperature to the core atoms. At the onset of simulation, both the core and the surface lose their kinetic energies to the potential mode as depicted by their lowering temperatures. Ultimately, the core settles at a temperature lower than its initial value as expected. However, the behavior of the boundary

is quite astonishing; it settles at a temperature even higher than its initial temperature. This implies a net gain of kinetic energy during the initial nonequilibrium dynamics of the boundary atoms. This is further depicted in Fig. 3b, which shows the temperature difference between the boundary and the core. This temperature difference shows large fluctuation initially, but at the end, it takes away some kinetic energy from the core. As the larger kinetic energy of the boundary is actually given away by the core during the evolution of the phase space towards the thermal equilibrium, there is an essential correlation between the temperatures of core and the surface.

4. CONCLUSION

In a nutshell, we demonstrate that for a small atomic system with free boundaries, the boundaries tend to gain larger kinetic energy and hence a larger temperature as compared to the inner core. Surprisingly, this state of steady temperature gradient corresponds to equilibrated condition even at the microcanonical condition. This is contradicting the intuitive view and can be attributed to asymmetric degrees of freedom of the atoms at boundaries and core. We hope that these observations can provide a new approach of studying the phenomena like melting point depression of nanoclusters and mechanochemical synthesis of nanomaterials.

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