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Negative heat capacity of Ar_{55} cluster

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Abstract

The solid–liquid phase transitions of Ar_{55} cluster was simulated by the microcanonical molecular dynamics and microcanonical parallel tempering methods using Lennard–Jones potential, and thermodynamic quantities were calculated. The caloric curve of cluster has *S*-bend. To understand this behaviour, configurational and total entropies were evaluated, and the dents on the entropy curves were noticed as the sign of negative heat capacity. The heat capacities were evaluated by using configurational entropy data. The potential energy distributions have bimodal behaviour in the given range at the melting temperature. At the same time by using configurational entropy canonical caloric curve and canonical heat capacity were calculated. To obtain entropy change upon melting, total entropy were calculated from the caloric curve. The microcanonical results melting temperature, latent heat and entropy change upon melting values were reported and compared with the values reported in the literature and the values calculated from the thermodynamic relations offered for bulk matter, consistent values were found.
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Keywords: Negative heat capacity; Solid–liquid phase transition; Ar cluster; Molecular dynamics; Parallel tempering

1. Introduction

Negative microcanonical heat capacity in clusters has been predicted theoretically [1–4] and experimentally [5–7] and attributed to the non-additivily of a cluster with finite size. Negative heat capacity may be interpreted as an increase in the total energy that causes a temperature reduction, a contradiction to every day experience. But negative heat capacities have since long been known in astrophysics [8,9], where energy can be added to star or star cluster which then cools down. A similar effect has been calculated for fragmenting nuclei [10,11]. The common feature of these very different systems is that the thermodynamics is non-extensive. The energy of such a system of *N* particles is not proportional to *N*. Moreover, it is important that the total energy is not simply the sum over the subsystem if the systems are divided into arbitrary subsystems. The interaction between the subsystems has to be taken into account. Consequently in clusters and nuclei, the interaction between subsystems is not negligible due to their small size. This peculiar effect has gained much interest recently since the experimental results for a negative heat capacity have been announced for the solid–liquid transition of 147-atom sodium cluster [7], and for the liquid–gas transition of hydrogen atom clusters.

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To understand the physics lying behind the *S*-bend behaviour of the caloric curve in the solid–liquid phase transition range is a challenging problem. To monitor the mechanism certain simulation techniques should be applied to microcanonical ensembles to mimic the phase transition and then related thermodynamic quantities should be calculated. Ar_{55} is a cluster known as showing *S*-bend behaviour in its caloric curve [2,12]. If microcanonical caloric curve has *S*-bend, the entropy curve has a dent with an inverted curvature that corresponds to negative heat capacity and the potential energy distribution of the cluster within the phase transition region shows bimodal structure [13,14]. In this study, to investigate the melting mechanism of the microcanonical ensemble, constant-energy molecular dynamics (MD) and microcanonical parallel tempering Monte Carlo (PT) simulation methods were employed and the multiple histogram method was used to calculate the thermodynamic quantities and the canonical ones to compare to those given in the literature.

One important question in the cluster physics is that whether one can use the thermodynamic relations offered for bulk matter [13] for the clusters? This question may be answered by evaluating some thermodynamic quantities. In this sense, the total entropy was evaluated by a technique proposed by Chekmarev [15] to compare total entropy change upon melting with the one calculated from the thermodynamic relation offered for bulk.

This paper is arranged in the following way: in Section 2, a computational method is described in detail. The results and discussions are given in Section 3. Section 4 provides a summary and a detailed conclusion of the study.

2. Computational method

The interactions between atoms in the cluster studied is described by the pair-wise Lennard–Jones (LJ) potential:

$$V(\{r_i\}) = \sum_{i<j} V_{ij}(r_{ij}), \tag{1}$$

where

$$V_{ij}(r_{ij}) = 4\varepsilon\left\{\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right\} \tag{2}$$

and $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$. The values for $\varepsilon = 1.67 \times 10^{-14}$ erg and $\sigma = 3.405\,\text{Å}$ are reasonable parameters for argon [16]. In this study, all results are given in the LJ reduced units ($\varepsilon = 1$, $\sigma = 1$).

The thermodynamical properties of solid–liquid phase transition for Ar_{55} cluster is extracted first from microcanonical MD simulations. Hamilton's equations of motions were solved by the LJ potential for all atoms in the clusters on a grid of total energies using Hamming's modified fourth-order predictor–corrector propagator with a step size of 5×10^{-16} s. The cluster was prepared with zero initial total linear and angular momenta and the initial co-ordinates were global minimum which obtained by simulated annealing method and is the same with that of listed in Ref. [17]. Trajectories of length of 2×10^6 steps were generated on a grid of total energies enough to observe the solid to liquid-like transition in the cluster. The total energy in the individual runs was conserved within 0.0001%. To sweep a whole energy range from ground state to liquid state, 38 simulations were performed with the energy step, which corresponds to the increase of temperature step ΔT by 0.015. Second from microcanonical PT simulations. Simulation runs consisted of 2.5×10^6 MC steps and 5×10^4 steps were used to thermal equilibrium. Twenty different total energies ranging from 4.53 to 90.67ε, corresponding to the MD simulation range, have been used, in addition to a constraining sphere of radius 3.8σ to prevent evaporation. For each total energy, potential energy values were saved and these results were used in the multiple histogram method [18,19].

In this study kinetic temperature T_K, configurational entropy, thermodynamic temperature, internal energy, microcanonical and canonical heat capacities and potential energy distribution were calculated.

The kinetic temperature of cluster is

$$T_K = \frac{2\langle K\rangle}{(3N-6)k}, \tag{3}$$

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