MELTING, FREEZING AND THE POTENTIAL ENERGY LANDSCAPE

BY

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1. Energy landscape
2. Solid - liquid phase equilibria

Certificate

This is to certify that the thesis titled " **MELTING, FREEZING AND THE POTENTIAL ENERGY LANDSCAPE**" is being submitted by **Mr. Somendra Nath Chakraborty** to the Department of Chemistry, Indian Institute of Technology, Delhi, for the award of the degree of **Doctor of Philosophy**. This thesis is a record of bona-fide research work carried out by him under my guidance and supervision. In my opinion, the thesis has reached the standards fulfilling the requirements of the regulations relating to the degree.

The results contained in this thesis have not been submitted to any other university or institute for the award of any degree or diploma.

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To my parents

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Abstract

This thesis focuses on computational studies of simple, one-component classical liquids and solids bound by isotropic pair interactions with steep, short-range repulsions. A combination of Monte Carlo (MC), Molecular Dynamics (MD) simulations and energy landscape analysis is used to understand thermodynamic and kinetic aspects of melting and freezing.

Chapter 1 presents an overview of those aspects of the literature of relevance to this work. Section 1.1 discusses the scaling laws correlating transport properties, such as diffusivity with excess entropy, defined as the difference in entropies of the liquid and ideal gas under identical temperature and density conditions. The relationship between thermodynamic behaviour at melting and the underlying features of interparticle interactions is discussed in Section 1.2. This section also discusses the simulation techniques available to estimate solid-liquid coexistence conditions. Melting and freezing rules which approximately predict solid-liquid coexistence from single phase properties are also summarised here. Section 1.3 summarises the classical theory of homogeneous nucleation in context of melting and crystallization. Potential energy landscape (PEL) analysis is a means to relate liquid state properties, including crystallization and glass formation, with the key features of the underlying multidimensional potential energy function. Section 1.4 describes three aspects of the PEL approach that are relevant to my work: instantaneous normal mode (INM), inherent structure and the stationary point (SP) analyses. The concluding section describes the organization of the thesis.

Chapter 2 deals with the computational details relevant to this work. Section 2.1 describes the model systems used in this work which are bound by the Lennard-Jones (LJ), smoothed Lennard-Jones (SLJ), Morse (M) and soft-sphere (SS) type of interactions. Variable range Morse systems are extensively studied in this thesis because they can be used

to mimic the correlation between range and curvature of the interparticle potentials seen in atomic systems. Computational details associated with the simulations, such as the periodic boundary conditions, are discussed in Section 2.2. Monte Carlo simulations are performed in canonical (NVT) and isothermal-isobaric (NPT) ensemble since these are the two ensembles describing the common experimental conditions. Description of the Monte Carlo simulations in these ensembles is provided in Section 2.3. While the Monte Carlo approach is convenient for obtaining static quantities, including thermodynamic observables such as relative free energies, it does not allow for the evaluation of dynamical quantities. In order to obtain dynamical quantities, microcanonical ensemble (NVE) molecular dynamics has been used at selected state points for some systems. NVE enesmble MD is discussed along with the energy conservation tests in Section 2.4. A brief discussion of molecular dynamics algorithms applicable in NVT and NPT ensembles is also provided in this section. Energy landscape analysis requires the use of local minimization techniques to identify minima and stationary points of the configurational potential energy functions. The final section gives the implementation details of the gradient-based limited memory Broyden-Flectcher-Goldfarb-Shanno (LBFGS) algorithm used here to locate minima.

Chapter 3 discusses the connection between thermodynamic, transport and potential energy landscape features studied for liquids with Lennard-Jones type pair interactions using both microcanonical molecular dynamics and isothermal-isobaric ensemble Monte Carlo simulations for stable liquids. The Dzugutov's scaling relationship for the diffusivity , $D^* = 0.049 \exp(S_2)$, holds for a wide range of simple liquids, where the exponential of excess entropy e^{S_2} gives a measure of the number of accessible configuration states of the system. The two particle entropy S_2 is extensively used in this thesis, hence the derivation of an ensemble invariant form of S_2, for a simple monoatomic fluid is given in some detail in

Section 3.1. Computational details are presented in Section 3.2. The instantaneous normal mode (INM) and stationary point (SP) analysis given in Section 3.3 and 3.4 respectively show that diffusivity depend linearly on several key properties of instantaneous configurations and saddle configurations- the energy, the fraction of negative curvature directions and the average, highest and lowest eigenvalues of the Hessian. Since the Dzugutov scaling law holds for these systems, the exponential of excess entropy shows a similar linear dependence on the the key features of instantaneous and saddle configurations.

Chapter 4 presents the study of solid-liquid phase equilibria in Morse systems, using free energy estimates of the relative stabilities of the solid and liquid phases. This chapter also discusses the relationship between structural order metrics and excess entropy of the liquid and identifies an excess-entropy based freezing criterion for simple liquids. Structural order parameters relevant for solids and liquids are discussed in Section 4.1. Obtaining the Landau free energy curves for melting of solids using umbrella sampling is discussed in Section 4.2. Section 4.3 presents computational details associated with implementation of the Landau free energy approach for Morse solids and benchmarks our procedure using well-studied Lennard-Jones system. Section 4.4 presents the application of this technique to Morse systems giving the coexistence conditions and the coexistence properties. At melting the relative change in density varies from 4% for soft, long range systems to 20% for hard, short range systems. The variation of these coexistence properties with range and softness of potential indicates that the phase transition properties at melting seem to be largely determined by the behaviour of the pair interaction near equilibrium separation while the long-range tail plays a more important role in determining the actual phase coexistence conditions. Morse systems seem to be a reasonable model which can be tuned to mimic the variation seen in atomic systems, from metallic systems with soft, long-range interactions to

van der Waals solids with short-range, strongly repulsive potentials. Relationship of excess entropy with structural order metrics is presented in Section 4.5. The pair correlation entropy is shown to have the characteristic $T^{-2/5}$ temperature dependence as well as a characteristic value of -3.5k_B at freezing. The characteristic value of -3.5k_B is applicable to a wide range of monoatomic liquids modelled by soft-sphere, Morse and Lennard-Jones type of interaction. This study helps to formulate a freezing criterion for these simple liquids, based on a single state property such as excess entropy.

Chapter 5 discusses the landscape-based freezing rule for systems modelled by smooth Lennard-Jones type of interaction. In this chapter, the relationship between thermodynamic properties and the energy landscape of the liquid is studied in the neghbourhood of the freezing transition to obtain a set of landscape-based criteria or rules for the freezing transition. Excess entropy and its relationship with inherent structure properties, inherent saddle properties and instantaneous normal mode properties are presented in Section 5.2, 5.3 and 5.4 resepectively. The exponential of excess entropy e^{S_2} gives a measure of the number of accessible states of the system and is also proportional to the diffusivity. Our results show that the ensemble average of a number of energy landscape properties as a function of $W = e^{S_2}$ shows a sharp change in slope at the freezing transition, allowing one to define landscape-based freezing rules. Examples of such properties are the configurational energy, configurational return distance and the average eigenvalue of the Hessian of inherent structures. Weaker signatures of freezing are also seen in instantaneous normal mode and stationary point properties.

Chapter 6 discusses the choice of an appropriate collective coordinate to understand melting process in solids. Section 6.1 describes the commitment probability analysis for forming the solid and liquid phases and the free energy study of metastability limits of LJ

solids. Results show that the second order global orientational order parameter provides a suitable representation of a collective coordinate to study melting. A qualitative prediction of the ease of nucleation of metastable phase is given in Section 6.2 from the barrier heights evaluated from the Landau free energy curves for Morse systems. Section 6.3 discusses the applicability of the local bond orientational correlation criteria to identify the solid-like clusters in a supercooled melt and shows that such criteria are adequate for systems with steep, short range repulsions, but for systems with softer interactions they may be inadequate.

Chapter 7 summarizes the principal conclusions of Chapters 3 to 6 and discusses the possible future extensions of this work.

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