

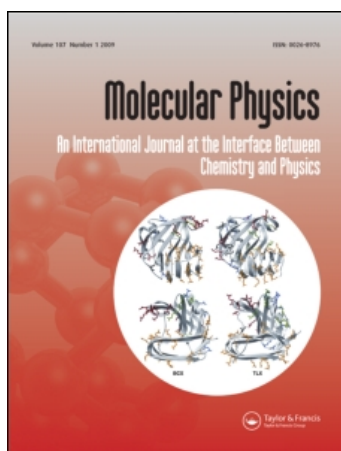
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### Molecular dynamics study of liquid-solid transition of dense Lennard-Jones liquid

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## Molecular dynamics study of liquid–solid transition of dense Lennard-Jones liquid

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We report a molecular dynamics simulation of solid–liquid phase transition. The system consists of 864 particles interacting with Lennard-Jones potential in  $N, E, V$  ensemble. A thermodynamic construction based on Helmholtz free energy surface is analysed and applied to the simulation data. It is shown that metastability limits can be obtained in this approach of simulation and a van der Waals type of loop in an  $E$  (internal energy) against  $1/T$  plot can be used to construct an equal-area plot to locate the melting temperature. The thermodynamic properties of the liquid and solid branches can be thus connected.

We use a Voronoi cell construction to present the configuration disorder of melting phenomenon from simulation data. Information entropy based on the distribution of Voronoi cell size and shape is calculated and compared with thermodynamic entropy of melting; the agreement is good. It is shown that instability associated with melting transition is mainly caused by change of shape of the cage volume in defect formation. Results of Voronoi analysis is consistent with the vacancy split-interstitial pair defect mechanism.

### 1. Introduction

Our present understanding of liquid–solid transition is still very limited [1]; there is no quantitative understanding of the physical mechanism for melting transition, magnitude of melting temperature, and entropy of melting even for the simplest atomic liquids. The structural diversity at the molecular level of liquid and the cooperativity of the melting transition make the problem a formidable challenge. In recent years, there have been two new approaches to the problem: the density functional theory and molecular dynamic simulations of melting transitions in small cluster systems. There has been some success recently using the density functional theory of inhomogeneous simple liquids [2–4]. A solid is considered as an inhomogeneous liquid and one can thus calculate free energy changes using ideas in liquid state theory. However, it is difficult to justify a thermodynamic expansion of solid state around liquid; furthermore density functional theory does not offer a physical picture of what is happening in the transition. Lovett [4] has offered a challenging critique of density functional theory with regards to phase transition applications.

On the other hand, molecular dynamics (MD) simulation does offer an opportunity to visualize the transition process. The works of Berry's group [5] have led to a detailed picture of the low-lying excitations of small clusters of Lennard-Jones particles that are relevant in the melting transition. However, it is still not clear how one can extrapolate from the small cluster studies to the problem of bulk melting. It would be highly interesting to re-examine the bulk melting transition by MD simulation with a view to extracting the physical mechanism of the process. Three problems face us

here. First, the ensemble chosen for study matters very much since it is the fluctuation behaviour that determines the coexistence region. Secondly, one needs to have a way of constructing the thermodynamic state functions, especially free energy and entropy. Thirdly, one needs to have a method for structural analysis to characterize the microscopic mechanism for melting transition.

The phase diagram of the Lennard-Jones (LJ) fluid has been studied [6–10] using MD and MC techniques. However, MD simulation of liquid–solid transition for even the simplest atomic liquid system is quite nontrivial. There is no easy way to estimate the free energy across the instability gap between liquid and solid. As the two-phase region is approached, large fluctuations are present and it makes the system dynamics slow. One has trouble continuing into the metastable region and reaching its limits.

Traditionally, in order to compare with experimental studies, most discussions of liquid–solid transition are done in canonical ensembles or constant  $T$ ,  $V$  ensembles, either by Monte Carlo [8] or by constraint molecular dynamics [10]. One then makes the analytical continuation either in free energy surface or by Maxwell equal-area construction in  $P$ ,  $V$  space. In contrast, detailed thermodynamic analysis of fluid–solid transition in constant  $V$ ,  $E$  is lacking although earlier computer simulation studies are often done in microcanonical ensembles. It is the purpose of this paper to show that microcanonical MD studies of the solid–fluid equilibrium can be fruitful.

In textbooks, it is often demonstrated heuristically that for a large system described by a microcanonical law, the state of a small subsystem is given by the corresponding grand canonical law. This is only true provided no phase transition is occurring. With phase transition, there are differences in fluctuations in different ensembles and one would expect the descriptions of phase transition and metastable states to be different in different ensembles. For example, even in simple chemical equilibria, it was shown by Zurek and Schieve [11] that the equilibrium concentration fluctuation deviates from the Poisson distribution (a grand canonical ensemble result) in a closed system. The deviation does not vanish at the infinitely large system limit. Bixon and Jortner [12], in a study of simple models for energy spectra of small clusters, established ensemble dependence of melting transition that reflects the differences in energy fluctuations between microcanonical and canonical ensembles.

Bulk phase transition is a phenomenon associated with macroscopic fluctuation and we would expect its description to be very different in different ensemble. In this paper, we choose to study the melting transition for LJ system in microcanonical ensemble. It will be shown that there are important advantages for constraining the system in constant volume and energy.

In canonical ensemble, coexistence between liquid and solid phases are determined by conditions of free energy which cannot be easily obtained in computer simulations. In the past, there were several approaches to this problem. Hoover and Ree [13] suggested a method of reversibly connecting the solid and liquid phases by constraining the particles within Wigner–Seitz cells to obtain the unstable and metastable solids. It is called the single-occupancy method. The path between any two thermodynamic states is accessible by a simulation method using the single-occupancy scheme. The method was used by Hansen and Verlet [6] to locate the first order melting transition for a Lennard-Jones system. These calculations are lengthy though, since many determinations of  $P(V, T)$  are necessary in order to do thermodynamic integration. In a second method, the coexistence condition can be obtained by direct simulation of the spatial coexistence of the two phases. Ladd and Woodcock [9] used this approach to simulate the coexistence of solids and liquids for LJ system. This

method requires a very large system and it is not suitable for a constant volume system.

We will show in this paper that melting transition can be profitably investigated in a microcanonical ensemble MD and a thermodynamic cycle construction in analogy of Maxwell construction can be made to locate the melting transition. The calculation is straightforward without the complication of a Wigner–Seitz cell construction in the single cell approach.

In microcanonical molecular dynamics (MD) simulation of liquids, we start from a crystal lattice configuration of molecular position and initial velocity distribution to let the system evolve. The initial structure will either stay as a thermalized crystal or melt if it has enough energy. The melting is rather quick, within one to several hundred vibrational period say, certainly much faster than the reverse crystal nucleation process if one starts from the liquid configuration. One can then obtain two branches of internal energy behaviour (against temperature) near the transition region. We will show that this relationship is enough for us to make a thermodynamic construction through the metastable region to locate the thermodynamic transition point. This is discussed in section 2.

There is another important advantage in studying liquid–solid transition in a constant volume ensemble. One can more easily focus on the structural distortion of the molecular arrangement while neglecting the changes in molecular motion. We would like to consider the liquid as a solid with additional structural entropy. The entropy is attributed to low lying structural instabilities in local molecular arrangement. Under constant  $T$ ,  $P$  transition, it is known that Lennard-Jonesium undergoes a relatively large expansion in volume and hence the average interatomic distances. One would then have appreciable contribution to entropy of melting owing to changes in phonon spectra (positive frequency). Recent study by Seeley and Keyes [14] shows that the positive frequency domain of local vibrations will be roughly constant provided the density of the particles remains the same. They also show that the negative frequency domain is important in structural instability in melting. Thus, for melting transition in a constant volume system, one is more concerned with the changes in geometric packing of the molecules.

Also, the dynamics of melting can only be investigated in microcanonical MD simulation. At constant  $T$ ,  $P$  MD, the dynamics themselves are somewhat fictitious in the sense that temperature relaxation is artificial. Only in microcanonical MD can we have detailed dynamics of phase transition in a real-time sense.

In this study, the method of characterizing structural change is mainly by the Voronoi analysis of the particle positions. This method is more suitable for identifying the local structure distortions in thermal excitations. From studies in small clusters [5], it is shown that the main excitation energies mostly come from local distortions of the nearest-neighbour distributions. Traditional analysis based on pair correlation gives rather too much emphasis to the long range structure. In section 3, we give a more detailed description of the Voronoi analysis we employed in this paper. Furthermore, we give an approximate calculation of the entropy of melting transition. It will be shown that the results are consistent with a simple defect mechanism of vacancy split-interstitial pair type.

In Section 4, we present the results of our simulation and analysis for a system at constant  $E$ ,  $V$  at the density of 0.965. We show the thermodynamic construction and results of structural analysis. Finally, in section 5 we discuss some possible future developments.

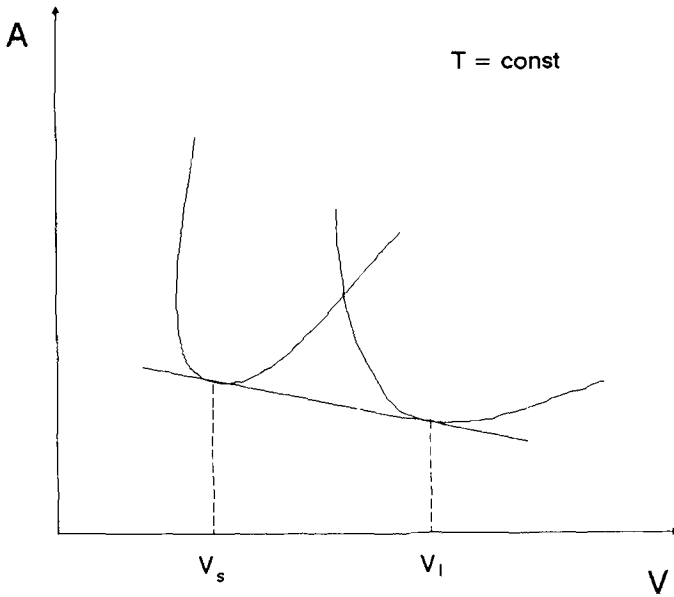


Figure 1. Schematic plot of isotherm of Helmholtz free energy. The double tangent construct is shown.

### 2. Thermodynamic construction

In this section, we give an analysis of the fluid–solid coexistence region in thermodynamics space. We consider a single component system at constant volume in the vicinity of the transition. Figure 1 gives a schematic plot of the Helmholtz free energy  $A$  against volume at constant temperature. The usual double tangent construction is also shown. In figure 2, Helmholtz free energy  $A$  is plotted against  $T$  at constant

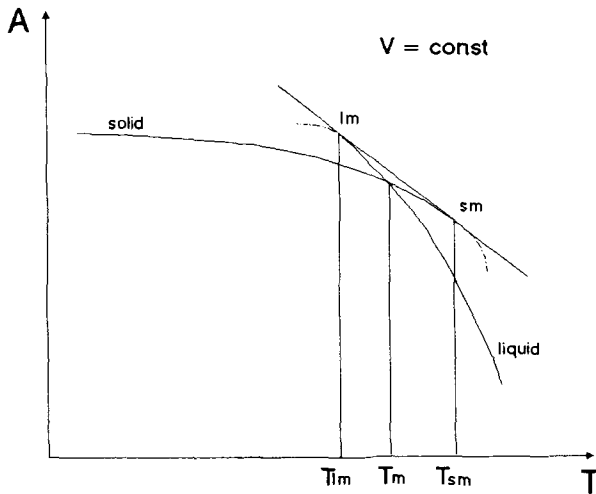


Figure 2. Helmholtz free energy against temperature at fixed density.  $T_m$  is the melting temperature. Metastable limits (sm and lm) are given by double tangents.

volume. The metastability limits are given by the common tangent condition,

$$(\partial A/\partial T)_{\text{sm}} = (\partial A/\partial T)_{\text{lm}}. \quad (1)$$

That is, the two limits are of equal entropy. We take the metastability limits being the limits of local stability. In a macroscopic  $T, V$  system, we would consider the local stability condition to be the one given by an isolated system (constant  $E, V$ ). For system states beyond the metastability limits, the entropy of the two branches will be reversed and locally the system will spontaneously transit to the other higher entropy branch when it traverses the metastable limit at constant volume and energy. The difference of Helmholtz free energy  $A$  at these two points (sm and lm) will be given by

$$\Delta A = (\partial A/\partial T)_V \Delta T = -S \Delta T. \quad (2)$$

Therefore the difference in internal energy  $E$  between these two limits will also be zero.

$$\Delta E = \Delta A + T \Delta S + S \Delta T + \Delta S \Delta T = 0. \quad (3)$$

We now examine a reversible thermodynamical cycle going through the metastable region  $T_m \rightarrow \text{sm} \rightarrow \text{lm} \rightarrow T_m$  in figure 2. The total change in Helmholtz free energy is zero for the cycle. At point  $T$ , the phase equilibrium condition  $\Delta A = 0$  can be written as,

$$\Delta E/T_m = \Delta S. \quad (4)$$

The right hand side of (4) can also be calculated through a tour along the two metastability branches. This can be obtained easily in a microcanonical ensemble MD simulation.

$$\Delta E/T_m = \Delta S = \oint_{\text{const } V} ds = \oint_{\text{const } V} C_V dT/T = \oint_{\text{const } V} dE/T. \quad (5)$$

Therefore an equal area construction in  $E$  against  $1/T$  plot will identify the transition temperature  $T_m$ . This is shown in figure 5 for our simulation data at density = 0.965 which we will discuss in the next section. In many cases, where  $T_{\text{sm}}$  and  $T_{\text{lm}}$  do not differ very much, the two branches in figure 5 appear to be nearly parallel. Then equal area construction implies that the melting temperature  $1/T_m$  will be located at the midpoint between  $1/T_{\text{sm}}$  and  $1/T_{\text{lm}}$ ,

$$1/T_m = (1/T_{\text{sm}} + 1/T_{\text{lm}})/2. \quad (6)$$

This does not differ very much from the formula,

$$T_m = (T_{\text{sm}} + T_{\text{lm}})/2. \quad (7)$$

used by Stillinger and Weber [15], and Chokappa and Clancy [10].

Briant and Burton [16] in a study of phase change of LJ microclusters ( $N < 100$ ) used an equal-area construction in a  $T$  against  $E$  plot; it is not rigorously justified but the resulting melting temperature is close to the prediction of (7). For LJ system at constant pressure, Streett, Raveche, and Mountain [8] made an equal-area construction on a van der Waals loop in  $P$ - $V$  space obtained by Monte Carlo simulation to locate the melting point. Their melting pressure is lower by 20% than that calculated by the indirect method by Hansen and Verlet [6]. The discrepancy was not resolved. Our opinion is that the metastability limits cannot be easily obtained in a constant  $T, V$  ensemble. One does not obtain a genuine small-system loop owing to the large energy fluctuation in a canonical ensemble.

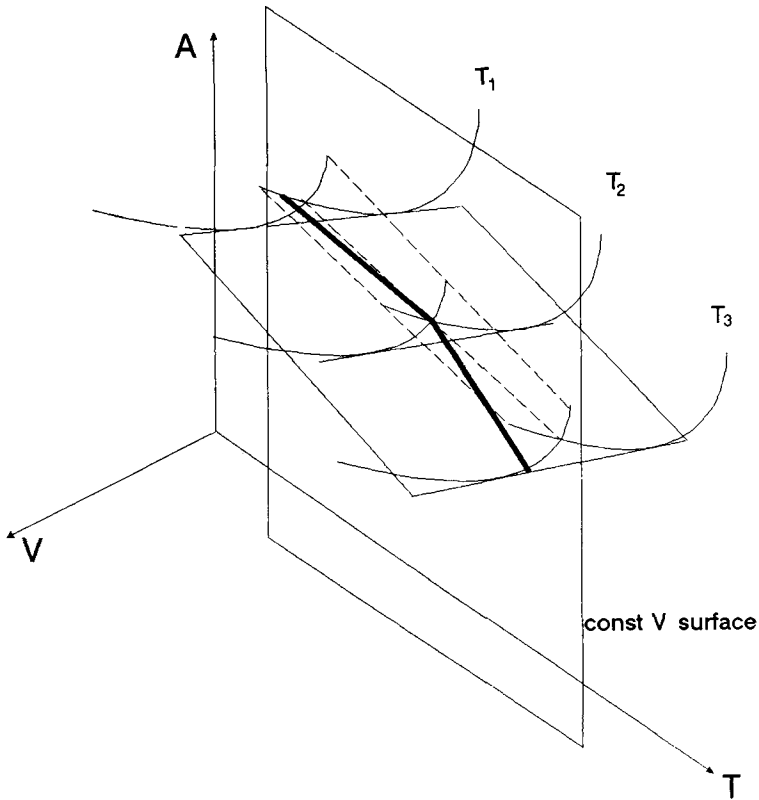


Figure 3. Helmholtz free energy surface in  $T, V$  space. Three isotherms at  $T_1, T_2, T_3$  are shown. The third solid line is the one shown in figure 2. Dashed lines connect  $T_m, T_{lm}$ , and  $T_{sm}$ .

In microcanonical simulation the two metastable limits in figure 3 can be obtained easily since the system, always conserving internal energy, will relax towards one of the two phases. With well chosen total energy, one can ‘force’ the system to evolve to one of the metastability limits. For total energy above  $E_c$  the system’s internal energy will converge to the liquid branch and for total energy below  $E_c$  the system’s internal energy will converge to the solid branch if the simulation time is long enough. There is no ambiguity. Our experience has been that the two metastability limits can be obtained in a relatively short computation time (details in the next section).

Our discussion up to now is for a constant volume system. For a constant pressure system, we can use a parallel analysis in terms of Gibbs free energy  $G$ , enthalpy  $H$ , and  $T$ . The result is that one can locate the melting point by an equal-area construction in an  $H$  against  $1/T$  plot. A simulation of the coexistence region based on constant  $H, P$  ensemble, similar to the approach used in this paper, would give the two state branches with loop. An equal area construction in an  $H$  against  $1/T$  plot would give one the transition point.

Combining figures 1 and 2, we obtain the free energy surface in  $T, V$  space shown in figure 3. We show here three isotherms to connect the surfaces. There are three connected surfaces in the transition region. The upper two surfaces (s and l) represent the solid and liquid branches where the third surface, constructed from thermo-

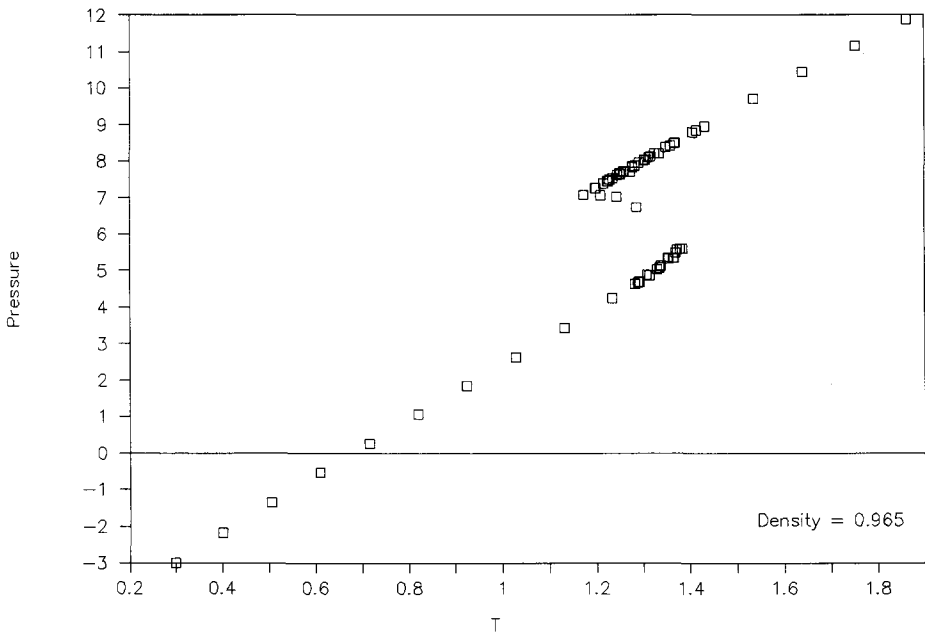


Figure 4. Pressure against temperature at a density of 0.965. The lower branch is solid and the upper branch is liquid state.

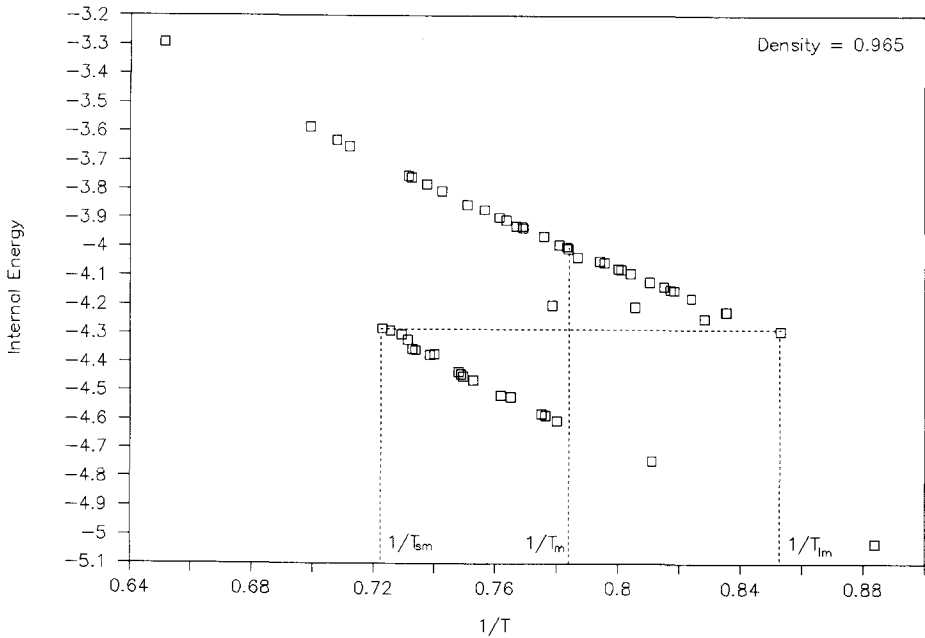


Figure 5. Internal energy against  $1/T$  at a density of 0.965. Equation (5) gives the melting point at  $1/T_m = 0.784$ .



dynamic criteria, is the common tangential surface of the above two surfaces. A constant volume section of the surfaces in figure 3 gives the curve in figure 2.

For a constant volume system in the coexistence region there are three time scales involved in the kinetic process starting from a chosen nonequilibrium initial state. Each one corresponds to a jumping of surfaces. In the first stage, of very short time, the system should relax locally to one of the upper surface to form a mixture of liquid-like and solid-like structures. In the second stage, one of the local region will dominate the other region so that the total system will be driven to a single surface (except maybe a small interfacial region) in the long time. In the very long time, the system can make another transition to the bottom surface (tangential plan in figure 3). So if one waits a very long time to the third stage, the whole first-order phase transition, under constant volume constraint, occurs reversibly and a finite temperature interval of phase coexistence should, in principle, exist. It implies that such a solid system melts reversibly at a lower temperature  $T_m$  than a cooling liquid would freeze reversibly at a higher temperature  $T_f$ . Since nucleation requires a very long time, such a third stage is not observed in computer simulation. One normally observes only the second stage in most of the computer simulations (as constant  $V$ ). Thus one would expect only to find a hysteresis transition temperature range between which the two states coexist. Also, one would be able to find a sharp temperature at which Helmholtz free energy surfaces intersect. This can be visualized in figure 3. This thermodynamic point can be found by the thermodynamic construction developed in this section based on MD simulation data. It is the purpose of this paper to discuss the melting transition in the second stage by microcanonical MD simulation.

### 3. Computational procedures

The MD algorithm we employed is quite standard [17]. We solve the  $3N$  coupled Newtonian equation of motion for an  $N$  classical particle system in a cubic box with periodical boundary conditions by the Verlet algorithm [18]. The particles interact with each other by a Lennard-Jones (6-12) potential. In simulation, the interaction cutoff is at  $r = 2.5$  and the potential is shifted upward to make it continuous at cutoff point.

We initially carried out a series of studies in the fluid phase using systems of 108 particles. However, the bulk of our calculations are performed for the condensed phase (at high density) of 864 L-J particles in a cubic box with periodical boundary condition. All units are in L-J reduced units. The starting configuration is the standard f.c.c. lattice and a Maxwell-Boltzmann distribution of velocity; the step size is 0.005. We discard the first 1000 thermalization steps and then the next 11 000 or more steps are used for performing thermodynamic data calculation and structural analysis. Since 95% of the MD simulation time is spent in force calculation, that subroutine is properly vectorized and we could achieve 127 MFLOPS speed on a Cray-XMP.

For structural analysis, we will employ the Voronoi cell construction. Using the Voronoi volume construction, we will discuss the entropy of melting based on a microscopic representation of free volume of a liquid and disordered solid. It is one of the older idea in liquid state theory. Free volume was originally proposed to account for the equilibrium properties of a fluid, but later it was also shown to play an important role in molecular transport, and glass transition [19]. Earlier molecular dynamics simulations of Lennard-Jones liquids [17] strongly suggested that there is a

cage structure in a sufficiently dense fluid which persists after many collisions. Nonetheless, the effect of caging is often not easy to discern when the MD data is presented through the customary correlation functions.

A first attempt at analysing the structure of dense random packing system of atoms in terms of local structures of packings was made by Bernal [20]. The method used by him is the Voronoi tessellation. Later, Finney [21] made a detailed study for hard sphere and L-J liquid in two dimensions.

Suppose we have a random array of atoms in three dimensions represented by solid dots denoting the centres of atoms. The positions of the nuclei define a set of points which determine a distinct divisions of the space volume into polyhedral regions separated by planar boundaries. The division is the Voronoi/Wigner-Seitz/cellular froth. This construction is uniquely defined, each boundary having the property that it is equidistant from the two nearest sites. In this paper, we use the Voronoi analysis algorithm of Tanemura, Ogawa, and Ogita [22].

The Voronoi analysis provides a conventional definition of what is meant by ‘neighbour’. If the Voronoi polyhedra associated with two particles have a face in common, they are said to be neighbours. This definition identifies 12 neighbours for f.c.c. For thermalized lattice or fluid structures, the number of neighbours ranges from 11 to 18. The distribution would allow us to identify a solid or liquid structure. A Voronoi cell is characterized by its volume and number of ‘neighbours’. For a collection of interacting L-J particles, both are distributed around an average value. Distribution of faces per cell gives the extent of distortion of the cell shape. We will use cell volume to represent the free volume concept for fluid and solid [23]. The difference of Voronoi volume and atomic excluded volume will be roughly the free volume for atomic motion. Precisely, according to Wood [24], the free volume of each particle,  $f$ , in a dense liquid is given by,

$$f = (v^{1/3} - v_0^{1/3})^3 \quad (8)$$

Here,  $v$  is the cell volume and  $v_0$  is given by the minimum volume per molecule given by  $v_0 = \sigma^3/\sqrt{2}$ . Originally, the free volume in (8) is an averaged system parameter instead of a variable. Here, we will treat  $f$  as a distributed variable and use it to calculate entropy of liquid and solid based on a modification of the free volume theory of liquids.

We will further make the assumption that distribution of shape (number of neighbours) and volume are independent, so that total entropy is given additively by,

$$S = S_0 + S_s + S_v, \quad (9)$$

where  $S_0$  is a temperature dependent part that is continuous across the melting transition,  $S_s$  is the entropy associated with Voronoi cell shape (neighbour) distribution and  $S_v$  is the entropy associated with Voronoi volume distribution. We consider first a random distribution of dots without any interaction; the distribution of Voronoi volume would not be uniform and given by  $p_i^0$ . Thus, the entropy contribution will be given by the Kullback-Leibler entropy,

$$S_s = - \sum_i p_i \ln (p_i/p_i^0). \quad (10)$$

The number of configurations of random distribution of Voronoi volume of size  $v_i$  and number  $N_i$  is given by,

$$W = \frac{N!}{\prod_i N_i!} \prod_i f_i^{N_i}. \quad (11)$$

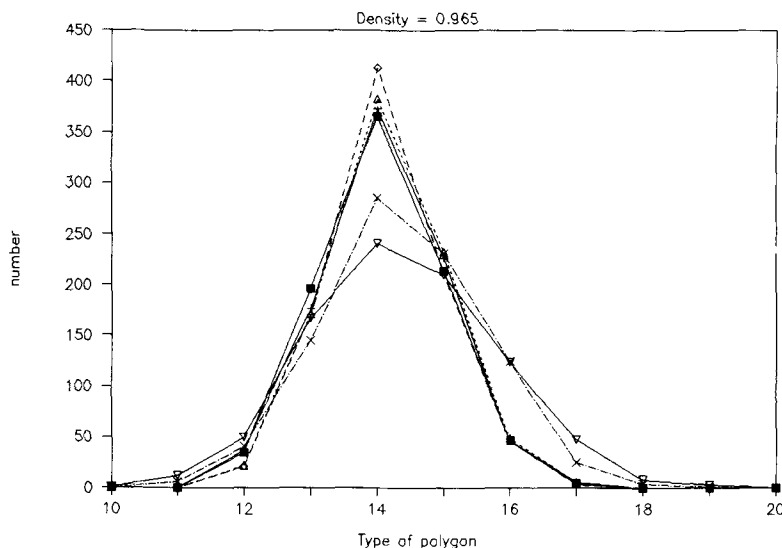


Figure 6. Voronoi cell shape analysis: distribution of faces per cell.  $\diamond$ ,  $T = 0.30$ ;  $\Delta$ ,  $T = 0.61$ ;  $+$ ,  $T = 0.92$ ;  $\blacksquare$ ,  $T = 1.23$ ;  $\times$ ,  $T = 1.32$ ;  $\nabla$ ,  $T = 1.64$ . The two highest temperatures are in the liquid state, the rest in the solid branch. The time steps are from 6000 to 11 000.

Thus, entropy owing to volume distribution would be given by,

$$S_v = - \sum_i p_i \ln (p_i/f_i). \quad (12)$$

Collins, Ogawa, and Ogawa [25] used the Voronoi geometric approach and Kullback-Leibler entropy of Voronoi cell distribution to express the entropy of an L-J liquid. With an adjustable parameter, their equations of state results were in substantial agreement with simulation data.

#### 4. Results of computation

Figure 4 presents computed values of pressure against temperature at density of 0.965. We can see separate branches for the low temperature solid and high temperature fluid states. Statistical errors in temperatures range from 0.005 at  $T = 0.30$  to 0.03 at  $T = 1.33$ .

Figure 5 shows the average energy per particle versus  $1/T$  (the caloric curve). In order to pinpoint the transition temperature accurately, by thermodynamic construction, many of the computations in the crucial transition region are run to 50 000 time steps. Thus errors in temperatures are reduced. As anticipated, the two metastable limits are isoenergetic; and the temperatures are  $T_{sm} = 1.38$  and  $T_{lm} = 1.17$  respectively. Discarding the few points that do not fall on the liquid or solid lines in figure 5, the thermodynamic equal-area construction (equation (5)) locates the melting point at  $T_m = 1.28 \pm 0.01$ . Equation (6) predicts a melting temperature  $T_m = 1.27$  while equation (7) gives  $T_m = 1.28$ ; they all practically agree with each other. The analysis in section 2 essentially convinces us they should give the correct melting point.

Figure 6 portrays the result of a Voronoi analysis of the number of planar boundaries from time 6000 to 11 000 every 50 steps at a density of 0.965 and various temperatures. It summarizes the results of Voronoi cell surface (number of planar

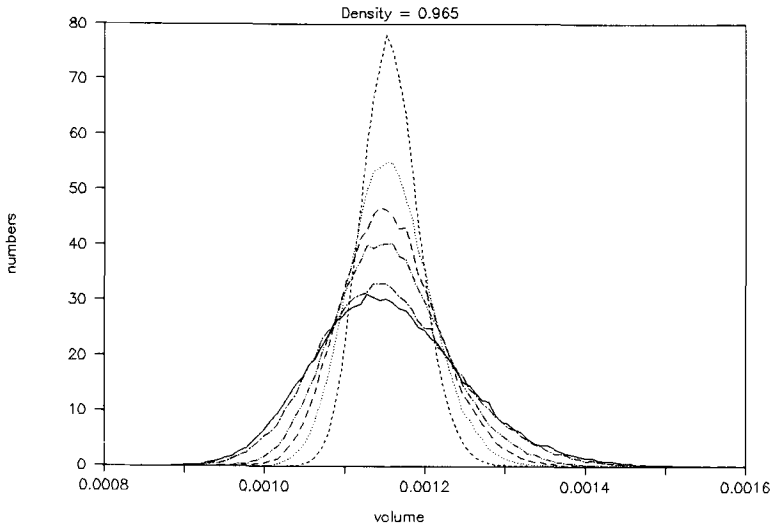


Figure 7. Voronoi cell volume analysis: distribution of cell volume. Conditions are the same as figure 6.

boundaries) distribution for selected state points. The low-temperature portion is in solid state of which the distribution of numbers of planar boundaries is relatively narrow and the maximum is at  $N = 14$ . The Voronoi polyhedra associated with a perfect f.c.c. crystal have exactly twelve faces, each with four edges. The broadening and shift to higher value of  $N$  is the result of thermal motion. The upper liquid branch is associated with a wider distribution of Voronoi shape. We can see that the transition from liquid to solid state occurs between  $T = 1.23$  and  $1.32$ .

Figure 7 gives us the Voronoi cell volume distribution. Again we see that the distribution is narrower for solid states than liquid states. For a liquid state, the distribution is slightly skewed towards the low volume side. It is interesting to see that for liquid state, the half width of volume size distribution is roughly  $1/14$  of the average volume per cell. Stillinger and Weber [26, 27], researching intrinsic defect structures, investigated a simple model atomic substance that freezes into a b.c.c. crystal by microcanonical simulation. They identified the low-lying instability in melting as creation of a vacancy, split-interstitial pair [8, 27]. This creation of a pair of defects would simultaneously give one larger and smaller Voronoi cell and the distribution of them would be thus broadened. A vacancy would make one empty cell volume to be shared by its neighbours, so each Voronoi cell of the neighbour of the vacancy would increase by the average  $1/14$  of the average cell volume. The split-interstitial defect would, on the other hand, decrease the cell volumes of its neighbours by about an equal amount.

Once the melting temperature is located, we can connect the thermodynamic functions between the two branches. Figure 8 gives the relative entropy function  $S$  over the temperature range; we put the entropy at  $T = 0.30$  arbitrarily to be zero. To get absolute entropy, it is not difficult to extend the calculation down to absolute zero. The entropy of melting at  $T_m$  is equal to  $\Delta E/T_m = 0.583/1.28 = 0.457$ . In comparison, the entropy of melting calculated theoretically by equation (9) is  $0.447$ , of which the contribution from  $S_s$  and  $S_v$  is  $0.295$  and  $0.152$  respectively. The changes

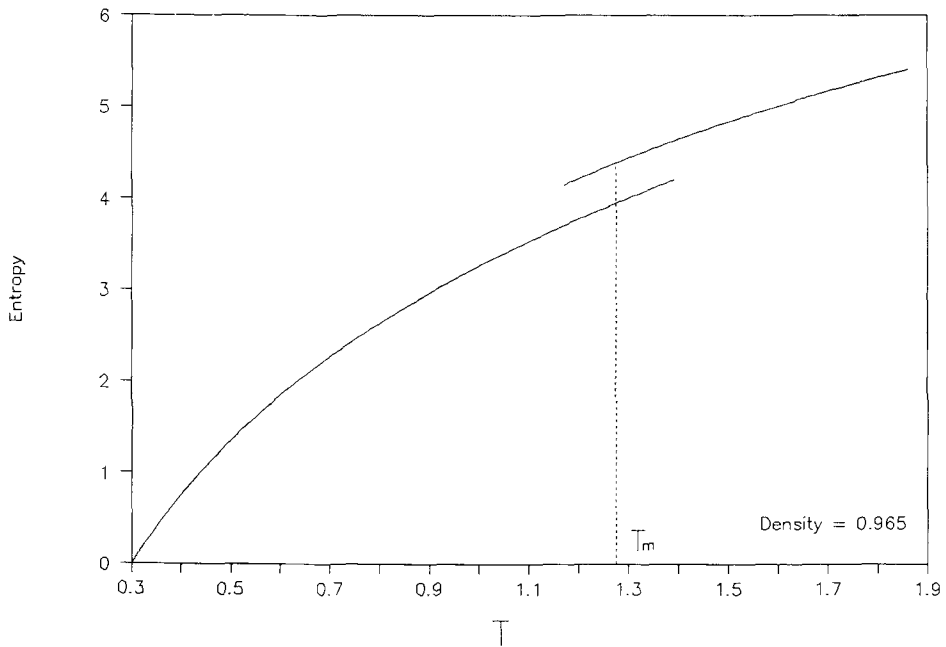


Figure 8. Entropy against temperature at density = 0.965. The entropy of transition is 0.457 at  $T_m$ .

of cell shape accounts for about 2/3 of the entropy of melting. The agreement is surprisingly good.

It seems that Voronoi analysis of cell size/shape distribution can account for most of the entropy of melting. We note also that the entropy of melting at constant pressure ( $P = 0.0$ ) is about 1.6 for the same system [10]. The difference is due to volume expansion upon melting and the resulting changes in the vibrational spectrum. In dealing with a constant volume system, the positive portion of the vibration frequency does not change upon melting roughly and we can focus better on the spatial arrangements of particles.

We also examine two states chosen near the ends of two liquid/solid branches, at  $T = 1.18$  (liquid) and  $T = 1.37$  (solid) to compare their structural difference. Figure 9 portrays the pair correlation functions. The first peaks of the pair correlation functions are almost identical; the distribution of nearest neighbour distance is about the same while long range structures are different. Figure 10(a) and (b) give the distributions of Voronoi cell shape and volume. Again, one can see that cell shape distribution gives the main contribution to entropy of melting. Thus we conclude that the melting transition is mainly associated with twisting of the nearest-neighbour distribution such that fluidity can result upon melting. It is consistent with the creation of a vacancy, split-interstitial pair mechanism in low-lying instability on melting as discussed above.

## 5. Discussions

In summary, we have examined the phase transition behaviour in a microcanonical ensemble for simple liquids. We have shown that there are important advantages in studying in the microcanonical ensemble. This is owing to the difference in fluctu-

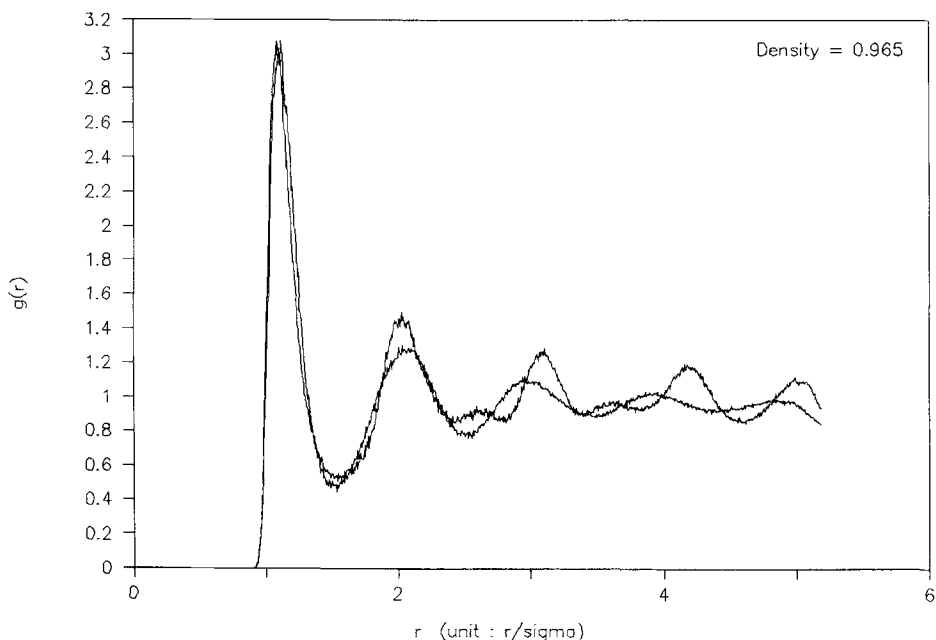


Figure 9. Pair correlation functions for liquid and solid at density of 0.965. The two cases are chosen near the ends of the metastability limits for the two branches. Temperature for solid is 1.37, temperature for the liquid is 1.18.

ation behaviour in different ensembles. This is particularly important for phase transition studies. Bixon and Jortner [12], in an analysis of models for melting in clusters, demonstrated that the transition gap in the caloric curve shows a marked difference for canonical and microcanonical ensembles. The hysteresis region in a caloric curve, when the temperature is varied up and down, exists only for the microcanonical ensemble calculation. Honeycutt and Andersen [28] report a marked difference in  $\text{Ar}_{13}$  clusters between their results of canonical systems and the data of Beck, Jellinek, and Berry [5(b)]. This difference, by itself, is of considerable methodological interests. It merits further study in the future. In a recent paper, Stodolsky [29] showed that in an adiabatic system local stability of a thermal system can be strengthened compared to an isothermal system. In principle, one could find a system that is metastable in isolation, but becomes unstable in contact with a thermal bath, even at the same temperature. From our analysis in section 2, we show that it is easier to reach the metastable limits in microcanonical ensembles and a thermodynamic construction can be used to build thermodynamic state functions across the transition region. In microcanonical simulation, the system converges to a unique state for a given total energy; there is no hysteresis when the total energy is varied up and down.

We should mention that the thermodynamic construction method employed in this paper should also be useful for nonspherical molecular system as long as the melting transition is fast enough for computation realization. The single occupation method of Hoover and Ree [12], however, is limited to very simple spherical molecules. Recently, Meijer, Frenkel, LeSar, and Ladd proposed a new method, based on perturbation potentials, for estimating the thermodynamic function for locating the boiling point of molecular liquid nitrogen [30]. It would be interesting to extend the

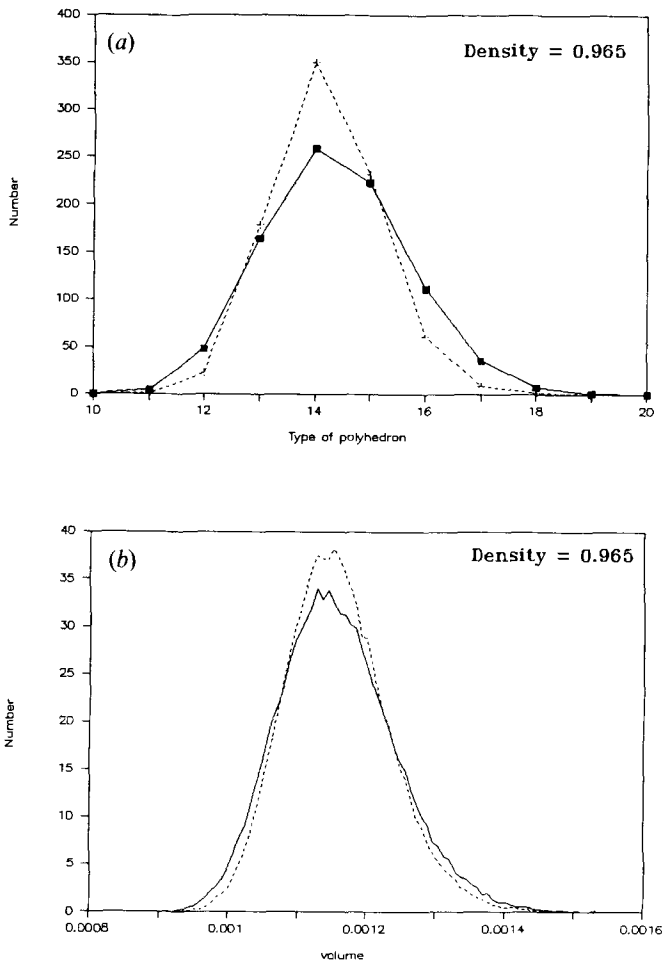


Figure 10. (a) Voronoi cell shape distribution at two points near metastability limits. Squares are for  $T = 1.18$ , and crosses are for  $T = 1.37$ . (b) Distribution of cell volume:  $T = 1.18$  (solid line), and  $T = 1.37$  (dotted line).

present method to diatomic system and compare it with the perturbation potential method.

Computer simulation of melting in two dimensions has contributed to our understandings of the mechanism of melting transition to a great extent [31]. Allen, Frenkel, Gignac, and McTague [32] studied a L-J system by MC and used Voronoi polygon construction to identify crystal defect structures prior to melting. Defects show up as pairs of five- and seven-sided polygons. The corresponding picture is not as clear in three dimensions because of the complexity of dislocation structures in 3D. We are dealing only with the statistical distribution of nearest neighbour arrangements in this paper. But, from the present study, we are able to identify the major contribution to the entropy of melting, that is, nearest neighbour orientation.

Primarily, the Voronoi maps give us nearest neighbour distributions where pair correlation functions describe the long range order. A theory of melting should deal with the interactions between the local defect structures leading to long-range disorder. At present, our knowledge of such a type of global behaviour for three dimensional

system is still lacking, although there is some recent progress in the theory of melting based on defect interaction [5(c,d)] and capillary phenomena [33] for melting in clusters. It will be of great interest if the present approach can help us build a bridge between the pictures for melting in small clusters and bulk crystals.

A very useful approach to structural change in melting transition would be finding the change of intrinsic structures and its energy spectrum. The hidden structure in liquids can be obtained in a Stillinger-Weber quench [34, 35] of molecular dynamics configurations. It would be interesting to analyze further the structure of liquid/solid in the transition region by this method. Combined with Voronoi analysis, the change in packing statistics of the melting transition can be better revealed. Further examination of the correlations between Voronoi cells would help us to identify the interactions between defects.

We also point out that a simulation of the coexistence region based on constant  $H$ ,  $P$  ensembles [36, 37] similar to the approach used in this paper would give the two state branches with loop and an equal area construction in an  $H$  against  $1/T$  plot would give one the melting temperature and pressure. Combined studies in  $E$ ,  $V$  and  $H$ ,  $P$  would give one the complete free energy surface structure of the system.

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