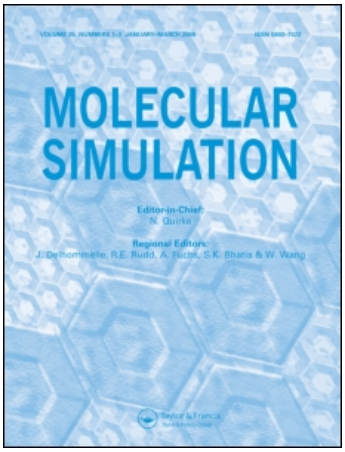

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Solid/Liquid Cluster Recognition in Heterogeneous Systems

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SOLID/LIQUID CLUSTER RECOGNITION IN HETEROGENEOUS SYSTEMS

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Criteria are presented which enable the differentiation between the extent of solid-like and liquid-like character in a heterogeneous system on a per atom basis. Such criteria are developed for two different interatomic potentials, the Stillinger-Weber model for group IV semiconductors and the Lennard-Jones model for insulators. For the Stillinger-Weber potential model, three criteria are presented: one based on the coordination number of nearest neighbors, one based on the three-body energy, and one based on the angular positions (spatial arrangements) of neighbors. For the Lennard-Jones model an angular criterion is used. The difficulties associated with the assignation of interfacial atoms (those with partial solid and partial liquid character) are discussed. The effectiveness of these criteria for both models is tested by application to the identification of solid-like nuclei in the melt.

KEY WORDS: Clusters, heterogeneous systems.

1 INTRODUCTION

Obtaining detailed rate information concerning the kinetics of crystal growth and dissolution processes from a dense fluid medium is a longstanding goal from both experimental and theoretical standpoints. Unfortunately, experimental probes of the early stages of crystal growth are currently not sensitive enough to capture information about these processes at the atomic level. While atomic-level computer simulation methods such as molecular dynamics would seem to offer a way to monitor these properties, the production of rate information requires that a numerical size of the growing (or dissolving) crystal be available as a function of time. An analysis of the atomic configurations produced by the simulation must determine which atoms belong to each phase at frequent time intervals, preferably each time step, since this number is directly related to the rate of growth or dissolution of the crystallite.

In a homogeneous system, it is straightforward to determine the phase of the entire

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system using properties such as order parameters, radial distribution functions, diffusion coefficients, etc. However, all of these methods produce an average value of the given property over the system (or even over small sub-regions), which is inappropriate for systems containing phase boundaries where properties may change over atomic dimensions and/or change quickly in time. The motivation for our studies is the determination of kinetic properties, especially the rates of crystal growth and dissolution. For this, we need criteria capable of identifying solid-like regions with an atomic-level "resolution". This is achieved by identifying individual atoms as having either a predominantly solid-like or liquid-like structure based on the characteristics of the surrounding atoms at that time instant. It is obviously meaningless to refer to an individual atom as being 'solid' or 'liquid' as these terms refer only to bulk phases. Issues related to the ability of structure alone to determine the "solidity" will be discussed later in the paper. Even the most carefully designed criteria are likely to be fraught with issues of subjectivity, particularly for atoms in the (usually diffuse) solid/liquid interfacial region that have partial characteristics of both phases. For purposes of large-scale computer simulation, one must also use a selection criterion that is mathematically and logically simple in order for efficient implementation.

In this paper, we shall consider the development of criteria to estimate the number of atoms belonging to a crystalline solid cluster in a surrounding liquid medium for two quite different interatomic potential models. First, we shall develop solid/liquid criteria for the Stillinger-Weber potential which was developed to model the behavior of group IV semiconductors such as Si and Ge. Second, we shall repeat this procedure for the Lennard-Jones potential, a widely used model for insulators. The applicability of these criteria is demonstrated for the case of identification of embryonic crystalline solids in a liquid, as for example would arise in crystal nucleation phenomena.

The organization of this paper is as follows. Section 2 describes past work to distinguish solid from liquid in a heterogeneous system. Section 3 gives a brief description of the simulation methods used. Section 4 is concerned with the development of solid/liquid criteria for the Stillinger-Weber (SW) potential. Section 5 describes the extension of these criteria for the distinction of solid atoms from liquid ones modeled using a Lennard-Jones (LJ) potential. Sections 4 and 5 also present results showing the application of the criteria to the monitoring of crystal growth and dissolution from the melt for both this SW and LJ potentials. Finally, section 6 summarizes our findings.

2 PAST WORK

Historically, most of the past work to distinguish between the phases present in a simulation has focussed on local structural variations. This approach works well where there is a large difference in the structural arrangements in the crystal and the liquid (*e.g.* for group IV semiconductors) but is more problematical for materials such as metals and insulators, which form very similar liquid and solid structural environments, particularly when one considers the relationship of one atom to its nearest neighbors [1]. For example, the number of nearest neighbors for a face-centered cubic (FCC) solid is 12; metallic liquids average 10–14. The density difference between solid and liquid metals is typically 1%, so that the change in nearest neighbor distance is negligible compared with thermal vibration. The first systematic

study of the local structure in a model liquid on a per-atom basis was performed by Bernal and Finney [2, 3]. Large numbers of ball bearings were placed in a container and the coordinates of the center of each one measured. This configuration was used to calculate a radial distribution function, and 'Voronoi polyhedra' were constructed about each center. The average number of faces and edges, the distribution of polyhedra volumes, and other properties were calculated and these statistics for the ball bearing model were used to quantify 'typical' FCC solids and liquids.

While the Voronoi polyhedra produce a measure of the local arrangement of the neighbors to an atom, it is a computationally expensive way to determine the phase of the material [4]. Other researchers have used a variety of local 'order parameters', whose value separates one phase from another. One widely used example is the 'distribution of cosines' method described by Haymet [5]. For the solid at 0 K, the distribution of the cosines of the angle between triplets of atoms, Ω, is non-zero only at a few characteristic values. As the temperature is increased, these spikes broaden into peaks, and in the liquid the distribution is smoothly varying. Figure 1 shows the solid and liquid distributions calculated for the LJ potential.

Haymet noted that a large variation in the distributions occurs at $\cos\theta = -1$ (linear triplets), which he speculated could be used to distinguish solid from liquid. Additionally, if the distributions Ω_S and Ω_L for the solid and liquid are known, he advanced as a plausible measure of the local order the normalized parameter

$$\bar{\Omega}(\cos\theta) = \frac{\Omega(\cos\theta) - \Omega_L(\cos\theta)}{\Omega_S(\cos\theta) - \Omega_L(\cos\theta)}, \tag{1}$$

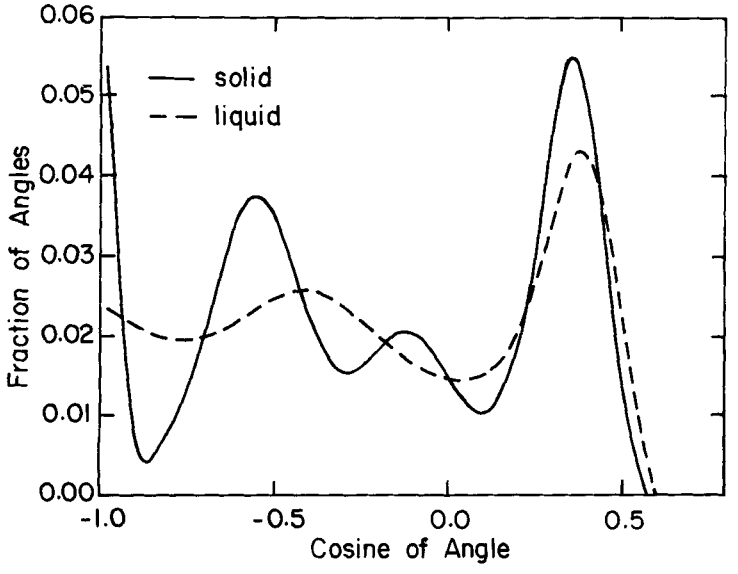

Figure 1 Distribution of the angular cosines between triplets of atoms for the Lennard-Jones potential in both the crystal phase (shown as a solid line) and in the liquid phase (shown as a dashed line). Taken from Haymet [5].

which could be integrated over all angles, as in Z, below, to determine the solid- or liquid-like character of the atomic environment.

$$Z = \int_{-1}^{1} [\bar{\Omega}(\cos\theta)]^2 d(\cos\theta) \tag{2}$$

The importance of using the cosine of the angle rather than the angle itself was "rediscovered" by Wicks and Mc Greevy [6].

There has been a considerable amount of research concerning the simulation of small clusters *in vacuo*, where "small" typically ranges from 7–200 atoms [7–11]. The melting of such small clusters, frequently containing so-called "magic numbers" of atoms, can display markedly different behavior to that of a crystallite in a bulk liquid phase, such as will be the focus here. Depending on the energy of the system, small clusters may oscillate between solid-like and liquid-like states over very short time-scales [7, 8]. This is not the case in the growth or melting of larger crystallites in the melt. An extensive study of the melting of small Lennard-Jones clusters has been performed by Quirke [9] who proposed the concept of a triplet angle distribution and used it to identify solid-like structure and to distinguish between different micro-crystal lattices. Of course, as pointed out by Berry and co-workers [8], for the smallest clusters, acquisition of solid-like structure is necessary, but not sufficient, to identify a true solid, which is distinguished both by structural and dynamic characteristics. Studies of small silicon clusters in the vapor have also been made [12–16].

In addition to the study of static structures, criteria to distinguish the extent of solid in a bulk liquid phase have found a natural application in the simulation of homogeneous nucleation and growth processes. A large number of methods have been employed to differentiate the extent of the various phases, but by far the most common methods of analysis has been the use of Voronoi polyhedra and of linear triplets. Voronoi polyhedra were used to determine the phase of a Molecular Dynamics (MD) configuration in early work on homogeneous nucleation for the soft sphere potential by Tanemura *et al.* [17, 18]. Local structure factors were used by Mandell *et al.* in early studies of nucleation in the LJ system [19, 20]. A thorough study by Mountain and Brown [21] to determine the relationship between the interatomic potential and the characteristics of the crystal nucleation was studied using the evolution of latent heat, the reduction in atomic mobility and certain orientational order parameters. Honeycutt and Andersen [22] performed a study on what they termed 'catastrophic crystal formation' (i.e. homogeneous nucleation and growth) observed in systems of 500 and 1300 LJ particles, where again the criterion used to differentiate the solid and liquid components in the system was based on the number of linear triplets. In this study, the solid atoms were defined as those which formed five or more linear triplets whose interior angle exceeded 162 or 165°.

The ultimate LJ study was performed by Swope and Andersen [23] in which a system containing 10^6 LJ atoms was analysed during homogeneous nucleation of crystal from the melt. The method used to determine solid from liquid was a combination of Voronoi polyhedra with small edge removal, and the 'inherent structure' method suggested by Stillinger and Weber [24]. The inherent structure is the quasi-minimum energy configuration about which the atoms are assumed to move, and can be uncovered by minimizing the potential energy of a given configuration via the steepest descents method. It was recognized that even the movement to the local minimum may require drastic rearrangement of the atoms so only partial

minimization was performed. This combination method was found to identify 97% of a bulk solid configuration at 75% of T_m as FCC, while a bulk liquid near T_m contained no atoms classified as solid. This criterion requires large amounts of post-simulation analysis in order to perform the steepest descents minimization, an obvious drawback particularly for large systems. The determination of solid and liquid fractions was therefore done only every 500 time steps, a frequency insufficient for rate studies. Hsu and Rahman [25-27] studied homogeneous nucleation in rubidium using LJ and other potentials to look for structural preferences in the nucleated phase. The formation of the solid was determined by Voronoi polyhedra with small edge removal, local structure factors, and by calculation of the distribution of cosines. Tsumuraya *et al.* [28] studied crystal nucleation from the melt using a long-range oscillatory potential for sodium. The structural changes were determined by Voronoi analysis and by the presence of five or more linear triplets. The authors concluded that the linear triplets method identified nearly the same atoms as the Voronoi procedure for the solid phase but required much less computation.

Solid/liquid criteria for models of semiconductors are surprisingly rare, considering the large number of studies of growth for these important materials. We are aware of only one such criterion, which was developed primarily for the computer graphics visualization of growth in SW models of Si, not specifically as a solid/liquid criterion [29]. This model, which we shall call the Grabow criterion, after its originator, designates an atom as being solid if it is four-fold coordinated and if three of its four neighbors are also four-fold coordinated. It will be shown that this criterion may be an overly stringent test of the extent of solid-like particles in a two-phase system.

It should be noted that all the past simulations of nucleation processes have used only structural criteria to determine the extent of the solid phase present. For crystal growth and dissolution processes, it is impractical to add a dynamic criteria (e.g. the calculation of the diffusion coefficient), however desirable, due to the difficulty of capturing the growth or dissolution in a timely manner relative to the collection of reliable statistics of a dynamic property. In our studies, to be described here, we have found that tiny solid-like clusters in the melt appear and disappear spontaneously on a fairly regular basis. It can easily be verified by classical nucleation theories that the probability of generating tiny clusters in the liquid increases as the size of the solid cluster decreases. However, such clusters typically do not survive for more than one vibrational period. Hence, they do not fulfill the characteristics (structure and persistence) regarded by Berry as pre-requisites for a "true" solid. However, once the cluster has increased in size (beyond around 40–100 atoms depending on the potential model and the temperature), the lifetime of these clusters is much longer (by at least an order of magnitude) and a structural criteria alone is sufficient. In the work that follows, for both Stillinger-Weber and Lennard-Jones potentials, we shall develop criteria based on a structural (and sometimes energetic) distinction of solid from liquid. As we have discussed above, this should be accurate for clusters larger than around 6 atoms for the SW potential and around 40 for the LJ potential (including the first interfacial shell). It has the advantage, relative to a Voronoi approach, say, of greater computational efficiency.

3 SIMULATION DETAILS

For both the studies involving atoms modelled using Lennard-Jones and Stillinger-Weber potential [24], seed crystals were implanted into a liquid phase, as described fully by Uttormark *et al.* [33]. The simulations were performed in the microcanonical ensemble where the number of particles, volume and total energy of the system are fixed (i.e. an NVE system).

For the Stillinger-Weber potential, a Verlet algorithm was used, with a system size ranging from 4,000–8,000 atoms. The simulations were carried out at zero pressure and a reduced temperature of 0.07 (for the dissolution studies) and 0.04 (for crystal growth). A time step of 1.5fs was used, providing energy conservation to 1 part in 10^5. For the Lennard-Jones studies, a Gear 5th-order predictor-corrector algorithm was employed, the system contained 13,500 atoms. The simulations were carried out at zero pressure and a reduced temperature of 0.45 to study crystal growth. A reduced time step of 0.004 was used. Periodic boundary conditions were employed on all faces of the cubic simulation cell. Since these boundary conditions are known to enhance crystallization for small system sizes, there was a need to use as large a system size as possible. The seed crystal must be surrounded by a large quantity of liquid to avoid the unwanted interaction of the seed crystal with its periodic image in the neighboring cells. In addition, for growth studies, the presence of the periodic boundary conditions placed an upper limit on the crystal size which can be grown for a given system size. The upper limit is reached when the seed crystal (and the surrounding interfacial shells) grows sufficiently large for it to interact with its image(s). Again, this required the use of a large system size.

The simulations of Stillinger-Weber atoms were performed on a Convex C210 machine. The Lennard-Jones systems were performed on IBM RS/6000 model 500 and Hewlett-Packard 9000/700 workstations.

4 SOLID/LIQUID DISTINCTION FOR STILLINGER-WEBER ATOMS

4.1 *Motivation*

The goal of this section is to describe the construction of criteria which differentiate the crystalline and liquid phases of atoms described by the Stillinger-Weber potential given only the instantaneous positions of the atoms. It is recognized that other information such as the particle velocities and the previous state(s) of the atoms may indeed be helpful in determining the phase boundaries, however, this information was not included in order to maintain simple, time-and space-efficient algorithms. These constraints were assumed so that methods could be developed for use in hardware-taxing MD simulations employing large numbers of particles and extending over large numbers of time steps. Given these constraints, information which could provide phase information must be contained in either the geometric arrangement of the atoms, or in the energetics of the interatomic potential which could be easily calculated from the given configuration. Thus it is appropriate to survey the various properties of the crystalline and liquid phases of the model material as a starting point for the construction of criteria.

Silicon possesses certain geometric characteristics which are clear starting points for developing solid/liquid criteria. In its semiconducting crystalline form, Si forms

a diamond cubic structure exhibiting four-fold coordination. Upon melting, the coordination changes significantly. The tetrahedrally-coordinated array of the solid is replaced by a liquid whose density is approximately 10% higher and whose coordination increases to 6–8 [30]. The SW potential reproduces this behavior. Solid and liquid configurations were prepared near the melting point and the radial distribution functions calculated. The number of nearest neighbors was found to be 4.2 and 7.5 respectively, determined by integrating the radial distribution function

$$N_n = \int_0^{r_n} dr\, 4\pi r^2 g(r)$$

where r_n was set close to the onset of the second peak in $g(r)$. Note that this definition includes some atoms which may have wandered into the normally unoccupied zone between the first and second nearest neighbors, particularly for the liquid phase where the second minimum is non-zero and broad. The change in number of nearest neighbors is the basis of the construction of the Grabow criterion.

The angular arrangement of the atoms in the liquid and solid phases is also quite different. In the crystalline phase, each atom forms the vertex of 6 equally-sized angles with its nearest neighbors. In the liquid, the angles vary substantially, and this difference was exploited for use in the Angular criterion.

Finally, the form of the interatomic potential used for the MD simulation of Si contains information which can be used to discriminate the solid from the liquid. The SW potential consists of two-and three-body interaction terms, which were included in order to promote the proper structure in the solid and liquid phases. It can be shown that a substantial amount of the potential energy stored in the bulk liquid comes from the three-body term, whereas energy is distributed mostly to the two-body interactions in the crystalline phase. This difference was used for the construction of the 3-Body criterion.

4.2 *The Grabow Criterion*

The Grabow criterion is an example of a coordination number based method: Solid atoms are defined as those with four nearest neighbors, three of whom also have exactly four nearest neighbors. In order to implement this criterion, one needs to define a nearest neighbor distance. Configurations of near melting point solids and liquids were prepared from bulk samples and it was determined that a nearest neighbor distance of 1.60σ was the most effective in classifying the known solid configuration as crystalline while labelling the smallest fraction of the liquid configuration as crystalline. The sensitivity of the criterion to changes in this parameter is discussed in section 4.7.

4.3 *The Angular Criterion*

An angular criterion was developed which can be adapted to any crystalline structure and which does not depend on a structurally dissimilar liquid phase. The motivating ideas for this criterion are as follows. For a given solid structure, the angles formed by an atom and all of its nearest neighbors are known (the atom in question resides at the vertex of the angles). In a rigid body, the deviation in the angle from the ideal value will be small, and in principle can be calculated if the vibrational range

of the atoms is known. In the liquid phase, the nearest neighbor distance may be identical to the solid phase, but the angular arrangement, particularly at large angles, acquires considerably more latitude.

Nearest neighbors around a central atom in a diamond cubic structure form six angles, all of which are 109° for the ideal lattice. Let Θ_i be the value of angle i. If we compute the sum

$$A = \sum_{i=1}^{6} \left(cos\ \Theta_i + \frac{1}{3} \right)^2, \tag{3}$$

A will be zero for the ideal lattice since cos 109° = $-1/3$. Deviations in the angles can only increase A due to the quadratic nature of the function. The 'cos' function was chosen since it is an easy value to compute from the atomic coordinates.

In order to implement this criterion, two values are necessary. First, the nearest neighbors need to be identified. The choice of 1.6σ for the nearest neighbor distance was made as before. Secondly, the largest value of A which defines a solid atom needs to be determined and a value of 0.4 was found to identify virtually all atoms in a known crystal configuration as solid and also rejected all atoms in a known liquid. The number of nearest neighbors allowed for a solid atom under this scheme was limited to four, although it is conceivable that five atoms could be arranged such that $A < 0.4$.

The extension to other lattices is slightly more complicated, since the angles formed need not all be equal. Given a structure which forms N ideal angles $\Theta_1, \ldots, \Theta_N$ each of which occurs $n_1, \ldots, n_N$ times, a possible candidate function is

$$B = \sum_{i=1}^{N} \sum_{j=1}^{n_i} (\cos\ \Theta_j - \cos\ \Theta_i)^2$$

where the angles formed in the actual configuration are Θ_j and the values of cos Θ_j have been sorted in order to find the 'best' matching cos Θ_i. It should be noted, however, that the variation in cos Θ_j for random, independent harmonic oscillators depends upon the equilibrium angle Θ_i about which the oscillations occur. It has been shown [31] that the expectation value $(\cos\ \Theta_j - \cos\ \Theta_i)^2$ is proportional to $C + \sin^2 \Theta_i$, where C is a function of the RMS deviation of the atoms from their equilibrium positions (and could in principle be found from data such as the Debye-Waller factor). Thus it might be argued that a better measure of the deviation from crystallinity is

$$B' = \sum_{i=1}^{N} \frac{1}{C + \sin^2 \Theta_i} \sum_{j=1}^{n_i} (\cos\ \Theta_j - \cos\ \Theta_i)^2$$

however this ascribes an equal weighting to each deviation in cos Θ_j, and it has been pointed out that the most telling deviations occur at large angles, i.e. for $\Theta_j \simeq \pi$. A general solution to this problem has not been found, and the difficulties associated with the application of angular criteria to the FCC structure are discussed further in Section 5.1.

4.4 *The 3-Body Criterion*

The difference in the distribution of potential energy between the two-and three-body interaction terms in the SW potential forms the basis for the 3-Body criterion. The

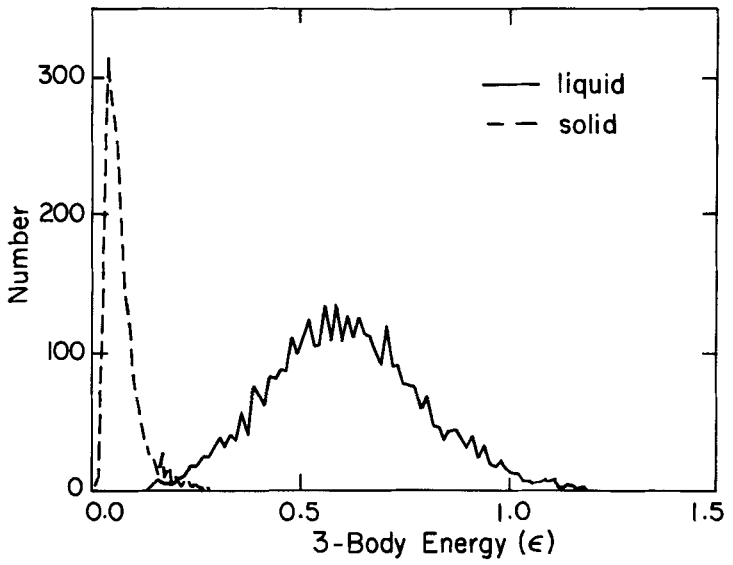

Figure 2 Distribution of the three-body energy (in units of ϵ, the depth of the potential minimum) for the Stillinger-Weber potential in both the solid phase (dashed line) and in the liquid phase (solid line).

three-body term essentially provides an energy penalty for deviation from a perfectly tetrahedral arrangement of atoms, thereby stabilizing the diamond cubic structure at low temperatures. Figure 2 shows the distribution of potential energy associated with the three-body term for solid and liquid phases. The two distributions overlap very little, providing a strong basis for distinguishing between the two phases. Crystalline atoms almost never exhibit a three-body interactions totalling more than 0.2ϵ, while the three-body energy of liquid atoms rarely drops below this value.

By itself, the value of the three-body interaction term is a reasonably good method for the determination of phase. However, it was found during the simulation of solid crystallites in the liquid that essentially spherical clusters with long strings of atoms attached to them would be identified as solid. This is probably due to the excessive tetrahedral order found in a SW liquid, a feature which has been identified previously [32]. By requiring that solid atoms also have 5 or less neighbors, this tendency was removed. With this additional refinement, the 3-Body criterion defines solid atoms as those with 5 or less neighbors within a radius of 1.6σ, and that have three-body interactions totalling less than 0.2ϵ.

4.5 *Identification of Significant Clusters*

The criteria described in the previous sections were designed to designate atoms as having solid- or liquid-like environments at every time step in a simulation of the dissolution of crystalline cluster in a bulk liquid. However, we found that small clusters of atoms (even individual atoms), unassociated with a central cluster, were frequently identified as having a solid-like environment at a given time and disappeared soon thereafter. Short lifetime tetrahedral orderings in a SW liquid are a known feature [32], thus the identification of solid-like atoms in the liquid for a given

configuration is not surprising. Since the likelihood of spontaneously generating a crystalline *embryo* (one which has a chance of growing to macroscopic size) even in a highly supercooled SW liquid is extremely low [34], it is more likely that these small clusters are unwanted manifestations of the criteria used to identify solid-like atoms. The identification of small transient clusters has also been found by Swope and Andersen in the Voronoi analysis of their data. The appearance of these insignificant clusters also has the practical problem of interfering with a count of the total number of atoms identified by the program as belonging to the principal cluster (whose size we were interested in monitoring).

In order to remove these transient clusters without adding to the storage burden of historical data, the following procedure was developed. All atoms in a simulation cell were identified as either solid or liquid and contiguous solid atoms were then grouped into clusters. Continuity was defined by the nearest neighbor distance, since each of the criteria contain this concept. Typically less than 10 clusters would be identified from a given configuration. It was found that most clusters consisted of less than 6 atoms, which were located more or less randomly throughout the liquid. These small clusters were reassigned to the liquid phase, leaving only 'significant' clusters. During the course of several hundred simulations where one cluster was to be expected, two non-trivially sized clusters were seen simultaneously only a few times. Instances of three coexisting clusters were not observed.

4.6 *Sensitivity of the Criteria to Parameter Changes*

The effect of changing the parameters on the size of the solid cluster identified by the various solid/liquid criteria was investigated. The Angular and 3-Body Energy criteria were very stable to changes in criterion parameters, exhibiting relative changes of up to approximately 10% for wide variations in the relevant constants. The Grabow criterion was the most sensitive: variation in the value of r_n from 1.4 to 1.6 produced cluster sizes which differed by a factor of 2. Table 1 shows the effect of changing the nearest neighbor distance on the number of atoms identified as belonging to the central solid cluster, as given by the 3-Body and the Grabow criteria. It can be seen that the choice of cut-off has a significant effect on the cluster size for the Grabow criterion, but the 3-Body criterion is relatively insensitive to this parameter. The Grabow criterion could be modified in order to make it more robust with respect to changes in the nearest neighbor distance, perhaps by requiring only 2 neighbors to be tetrahedrally coordinated for an atom be called solid, but

Table 1 The effect of the choice of nearest neighbor distance on the number of solid atoms identified by the 3-Body and Grabow criteria.

Cut-off distance (in units of σ)	*3-Body Criterion*	*Grabow Criterion*
1.6	177	75
1.5	185	141
1.4	187	200

Note: The temperature of the system of 4000 atoms is 1940 K. The results are shown after 4000 timesteps (*i.e.* 2 ps).

this is essentially equivalent to forming a new criterion and will not be discussed further here.

4.7 *Comparison of the Three Criteria*

As was pointed out earlier, criteria which attempt to distinguish liquid from solid fractions on a per-atom basis are inherently subjective. However, certain systematic differences in the identification properties of the criteria were observed. In particular, for the case of quasi-spherical solid clusters in the melt, the Grabow, Angular and 3-Body criteria identified a common region as being solid, but differed as to the extent of the solid outside of this region. The Grabow criterion provided a rather conservative description of the solid-like region. As can be seen in Table 1, the Grabow criterion identifies many fewer atoms as being solid than the 3-Body criterion. From this information as well as visual comparisons, it was recognized that the Grabow criterion is a very simple, computationally inexpensive way to determine the center of a crystalline region, but may exclude portions of the interfacial region which may be more crystalline than liquid. To use a metaphor suggested by Weber and Stillinger for the ice-water interfacial system [35], the Grabow criterion describes the 'core' but not the 'mantle' of the solid.

The 3-Body Energy criterion occupies the other extreme, classifying not only the same central region as solid but also an interfacial boundary layer between solid and liquid whose width is somewhat less than two atoms, in agreement with the findings of Broughton and Abraham for planar interfaces [36]. They found the width of the (111) and (100) interfaces to be between zero and two "layers" thick. The Angular criterion resides somewhere in-between the Grabow and 3-Body criteria in the extent of its inclusion of the interfacial region.

The result of using each of the three criteria to a simulation of the dissolution of a cluster in the melt is shown in Figure 3. While it is apparent that the criteria differ in the numerical size of the cluster at a given time, certain features are common to all three data sets which support the assumption that the criteria are indeed following the evolution of the same cluster. In another paper [33], we have shown that the three criteria can be rescaled relative to the Grabow criterion, differing only in the width of the interface identified by the criteria. As shown in Figure 4, the rescaling produces results in which the criterion dependence is small. It is therefore concluded that, due to the relatively sharp interface formed by this material and the large disparity between solid and liquid characteristics, the choice of criterion is not particularly crucial. The criteria can also be used to follow the growth of a SW crystal at sub-T_m temperatures, see Figure 5.

5 SOLID/LIQUID CRITERIA FOR LENNARD-JONES ATOMS

In some respects, the selection of criteria to differentiate crystal from liquid on a per-atom basis is particularly easy for SW models of materials. The presence of the three-body potential energy is a relatively unambiguous 'marker' of the phase of the system, even when considering only individual atoms. In addition, SW models do not have a particularly diffuse solid/liquid interface. Lastly, the large change in coordination number between solid and liquid is anomalous. As mentioned above, most materials show little change in coordination number on melting.

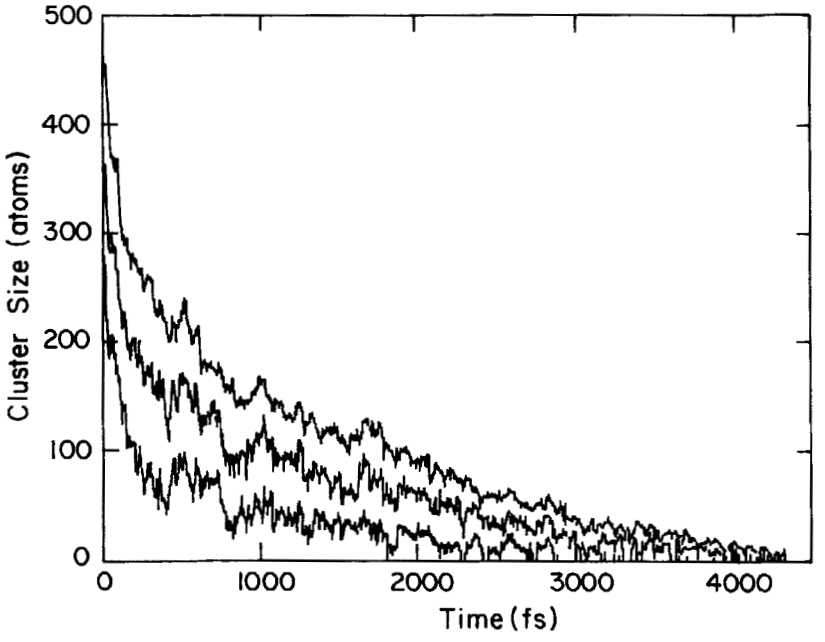

Figure 3 The time evolution of the size of an implanted crystalline cluster of Stillinger-Weber-modeled atoms, as produced by the 3-Body criterion (upper curve), Angular criterion (middle curve) and Grabow criterion (lower curve), showing the effect of the criterion on the raw simulation data for dissolution. The reduced temperature of the system was 0.07 (i.e. just above the melting point).

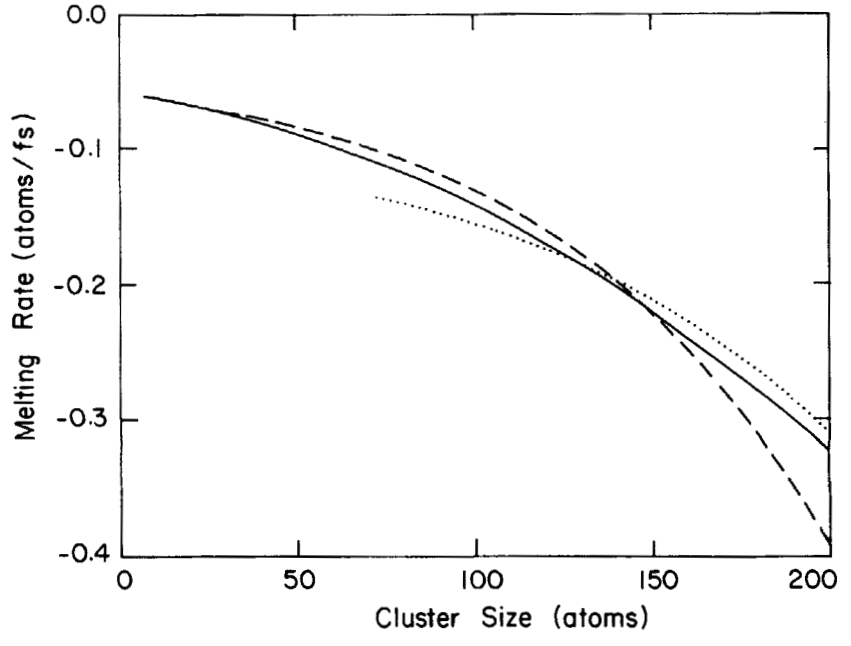

Figure 4 Results for the melting rate as a function of cluster size showing the similarity of the results once the raw simulation data for the three criteria has been rescaled according to the width of the solid/liquid interfacial region. Results for the 3-Body criterion are shown as a solid line, those for the Angular criterion as a dashed line and those for the Grabow criterion as a dotted line. The reduced temperature of the system was 0.07.

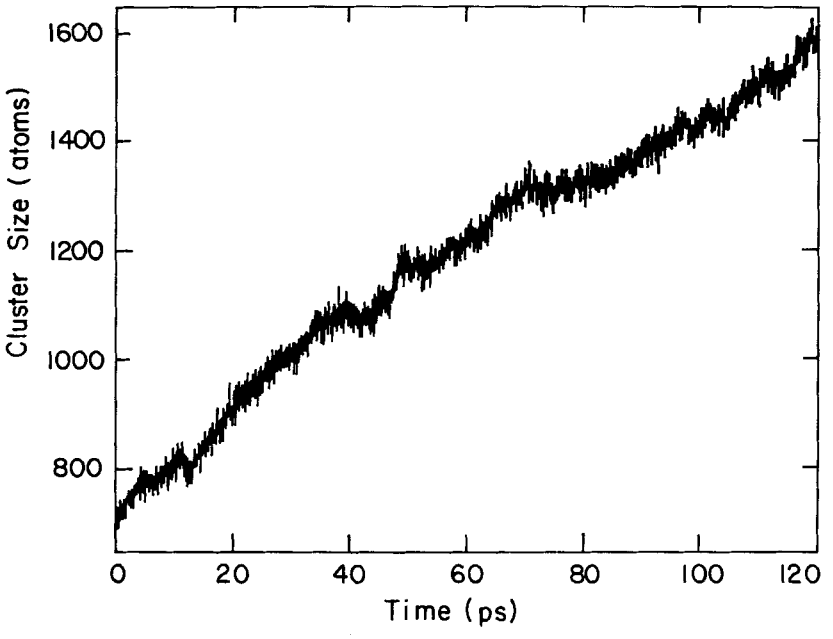

Figure 5 Results for the growth of an implanted crystalline cluster of Stillinger-Weber atoms as a function of time. The initial size of the cluster was 570 atoms in a liquid phase containing 5700 atoms. The post-transient temperature of the system was 0.04 in reduced units (around 70% of T_m).

It is interesting to speculate, then, whether it would be possible to obtain criteria to differentiate crystal from liquid in another material, one in which the differences between the two phases were less marked. An obvious test case in this regard is a consideration of the LJ model. This model has the advantage of being one of the most widely studied interatomic force models, for which a lot of information about the solid/liquid transition is available. It also has a small change in coordination number between crystal and liquid: the 12-fold static coordination of the solid is replaced by a 10-14-fold dynamic list of neighbors. Lastly, the relative diffuseness of the solid/liquid interface adds a new complication to the distinction between solid and liquid. It will be necessary to consider which (if any) of the interfacial atoms should be considered as being part of the crystal structure in the heterogeneous system of solid and liquid.

5.1 *An angular criterion for LJ*

In section 4.3, we noted that the angular criterion was developed with the intention of applying it to crystalline structures other than the diamond cubic structure. Unlike the diamond cubic structure in which all the angles formed by the nearest neighbors are 109° in the perfect lattice, the face centered cubic structure formed by LJ atoms is characterized by four different angles. As for the SW atoms, the first step in developing a criterion for the LJ system is to define a characteristic radius inside which the nearest neighbors can be found. Again, the position of the first minimum, T_n, in the pair distribution function was used for this purpose. As this minimum is non-zero, it is possible that this choice of r_n may miscount the number of nearest neighbors; this will be investigated later in the section.

In a perfect FCC lattice, there are 66 angles formed between triplets of atoms (i.e. the angles that all the nearest neighbors form with a central atom). Of these angles, 6 have a cosine of -1.0, 24 have a cosine of -0.5, 12 have that of zero and 24 have the value 0.5. In practise, we considered the squares of the cosines to avoid the computational penalty of taking a square root, and kept the sign of the cosine in the result:

$$sign(cos\ x)cos^2x\ = sign(\mathbf{r}_{ij}.\mathbf{r}_{ik})^2/(r_{ij}^2 r_{ik}^2), \tag{4}$$

The distribution of the squares of the cosines (keeping the sign) are presented in Figure 6 for both the crystal and the liquid. The bin width used to gather the

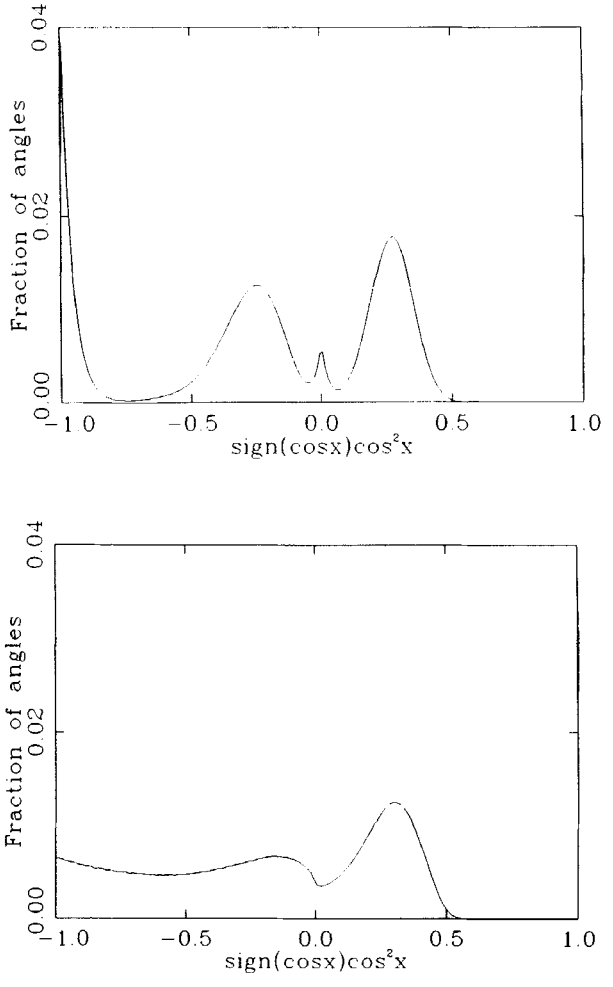

Figure 6 The cosine squared distribution between triplets of Lennard-Jones atoms for the solid phase (upper diagram) and the liquid phase (lower diagram) at a reduced temperature of 0.60. The distribution for the solid is divided into four regions A–D, separated by the minima in the function. The bin width used to collect the data for these figures is constant in cos x.

data for the histograms in constant in cos x not $\cos^2 x$ [6]. The similarity of this function for liquid and solid is considerable.

Determination of an angular order parameter

The small variation in the angular cosine squared distribution for the solid and the liquid needs to be enhanced to allow the differentiation between the two phases. The method we chose was as follows: First, the [sign(cos x).$\cos^2 x$] distribution for the FCC crystal lattice was classified into four regions separated by the minima in this distribution (see Figure 6). For each atom, the following steps were then taken:

(i) Values of sign(cos x) $\cos^2 x$ were calculated for all the triplets that an atom forms with pairs of nearest neighbors. These values fall into the four different regions of the distribution defined above.

(ii) For every one of the values (of sign(cos x) $\cos^2 x$) calculated, the position of the maximum corresponding to the region in which it belongs was then subtracted and the result squared.

For example, if a value of this function of 0.95 was found, this falls in the left-most region of the distribution in Figure 6. The maximum for that region occurs at -1.0, hence after subtraction of the position of the maximum and squaring the result, we obtain a value of 0.0025. These numbers were added together to produce an angular order parameter which we have denoted as F. At this point, the weight assigned to each of the four regions in the angular distribution curve was the same. Simple tests of the effect of weighting different region unequally, suggested that the parameter F is not particularly sensitive to the weighting scheme. Using the prescription above, the value of F is zero for an atom in a perfect FCC lattice. For

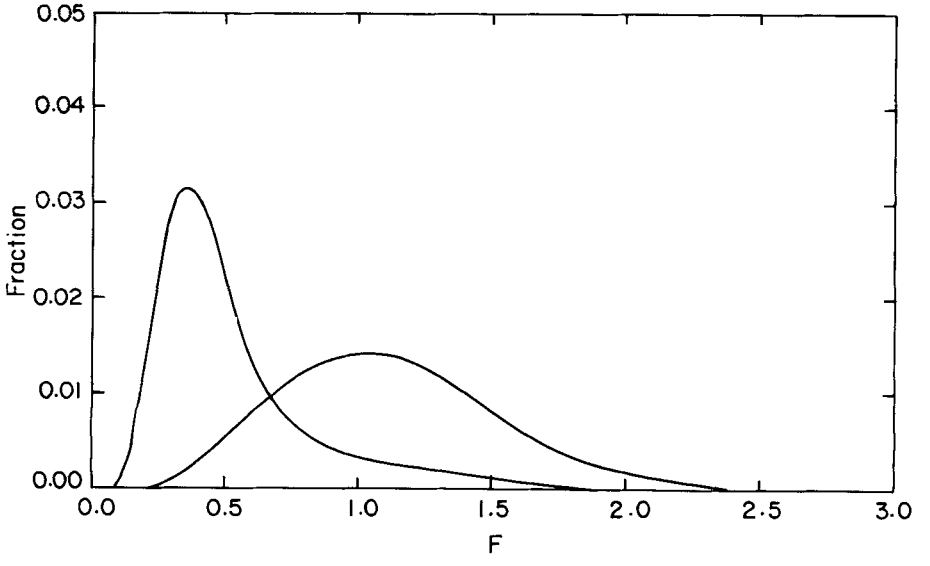

Figure 7 Distribution of the angular order parameter, F, for the solid (exhibiting a maximum at F = 0.4) and the liquid (maximum at F = 1.1) at a reduced temperature of 0.60.

the thermally-averaged positions of a typical lattice, the value of F will be between zero and that for the liquid; see Figure 7. Comparison of Figure 7 to Figure 2 indicates that the separation of solid-like from liquid-like environments in a LJ system of atoms will be more ambiguous than for the SW system.

Calculating the value of F which distinguishes solid from liquid

The first step is to perform simulations to produce an equilibrated solid and an equilibrated liquid at the same temperature. Here we used the modified LJ potential of Broughton and Gilmer [37] to determine the interatomic forces. The densities used for these two simulations are such that the pressure in the two systems is the same (i.e. the densities are different); zero pressure was used here. Using several different configurations for both the solid and the liquid, the angles between triplets were calculated and, hence, the angular order parameter, F, for each atom was evaluated. A large number of configurations should be used to obtain the distribution of F values; we used 100 configurations at different times for a system containing 2048 particles at zero pressure and reduced temperatures from 0.35 to 0.60 to produce the data for F shown in Figure 7.

A critical value of F, called F_C, was established as the single quantity used to separate solid-like atoms from liquid-like ones. Since the two distributions for F in the solid and liquid overlap, it is not possible to get complete (unambiguous) separation of the two phases. However, one can use the data to obtain a value of F that gives the largest possible separation for a given phase (solid or liquid), or the point where the two curves intersect or any other convenient criterion. We chose to select the value of F corresponding to the intersection of the solid and liquid curves as F_C. As an example of the kind of results this method produces, we found that, at a reduced temperature very close to the melting point ($T^* = kT/\epsilon = 0.60$), the method recognized 80% of a bulk (100%) solid system and confused 14% of a bulk liquid system as being solid. A recognition capability of 80% is insufficiently accurate for most applications and the criterion has to be improved by consideration of more subtle effects. These are described in Appendix A. The final scheme used to distinguish solid from liquid had an almost 100% recognition ability in heterogeneous solid/liquid systems of LJ atoms.

5.2 *Classification of Interfacial Atoms*

The planar solid/liquid interface for the LJ potential is well known to be diffuse, extending over several atomic 'layers' [37–39]. In order to decide the extent of the crystalline cluster, it is necessary to decide which (if any) of the interfacial atoms are sufficiently solid-like to warrant inclusion in determining the extent of the solid cluster. The distribution of angular cosines for the first and second interfacial "shells" are shown in Figure 8, where they are compared to those for the crystal and the liquid. The first interfacial shell is denoted as that closest to the crystalline core. At first sight, the results shown in Figure 8 suggest that *both* of the interfacial shells are more liquid-like than solid-like and hence should not be counted as belonging to the crystalline 'core'. However, when the positions of the atoms in these interfacial positions were inspected using a computer graphics visualization, a different picture emerged. Figure 9(a) shows the shape of the underlying crystal core (denoted by red atoms) and the positions of the first interfacial shell (shown in blue). The 'blue' atoms are almost perfectly aligned on FCC sites corresponding

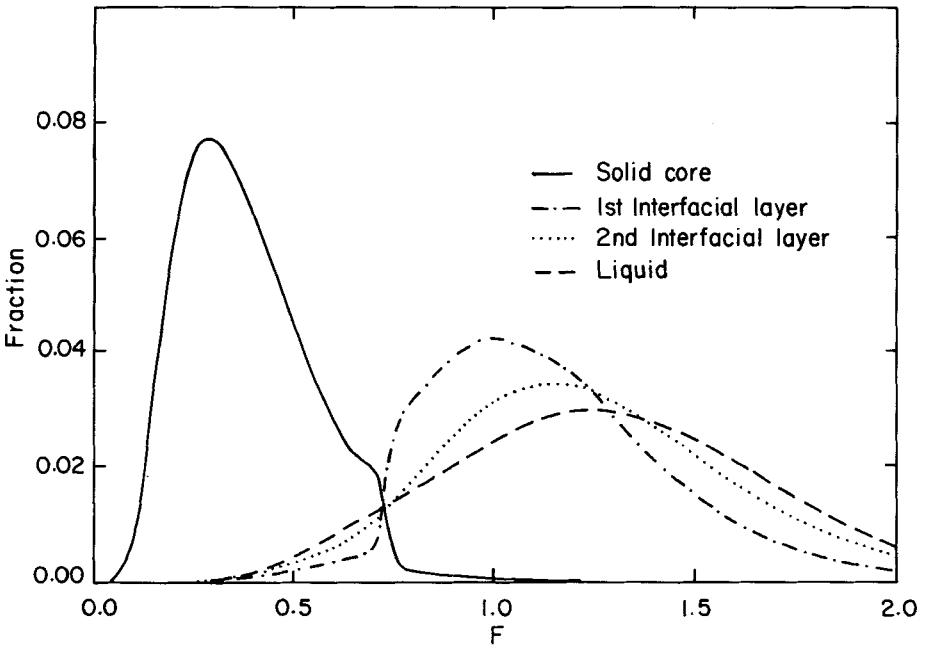

Figure 8 Distribution of the angular order parameter, F, for the underlying crystalline core (solid line), the 1st. and second interfacial shells (dot-dashed and dotted lines, respectively) and the liquid phase (dashed line) at a reduced temperature of 0.45.

to those constituting the underlying crystal (shown in red). Figure 9(b) shows the positions adopted by the second interfacial shell of atoms around the cluster; these atoms are shown in yellow. We have observed that the arrangement of the atoms in the second interfacial shell is quite different from that of the first interfacial shell and the central solid-like core. In general, the 'yellow' atoms appear quite disorganized except on some of the (111) surfaces. When viewed from above the (111) plane, some of the 'yellow' atoms appear to be organized in a crystalline fashion; see Figure 9(b). However, a closer study of their positions viewed from the (110) plane showed that the 'yellow' atoms were not located on FCC lattice positions. Frequently, they were located on positions corresponding to a stacking fault (in HCP-like positions relative to the 'red' and 'blue' layers beneath them). Since the atoms in the second interfacial shell were not always in FCC positions, nor were they classified as solid-like except their distance to the core, we excluded the second interfacial shell of atoms from being counted as part of the solid cluster. Here we limit our identification to FCC-like atoms; we are in the process of extending this method to include identification of HCP-like atoms.

As observed for the Stillinger-Weber potential, many transient clusters containing <40 atoms (including the first interfacial shell) were observed. As noted for the SW potential, the lifetime of these clusters was short, hence such clusters were not considered as constituting a significant cluster.

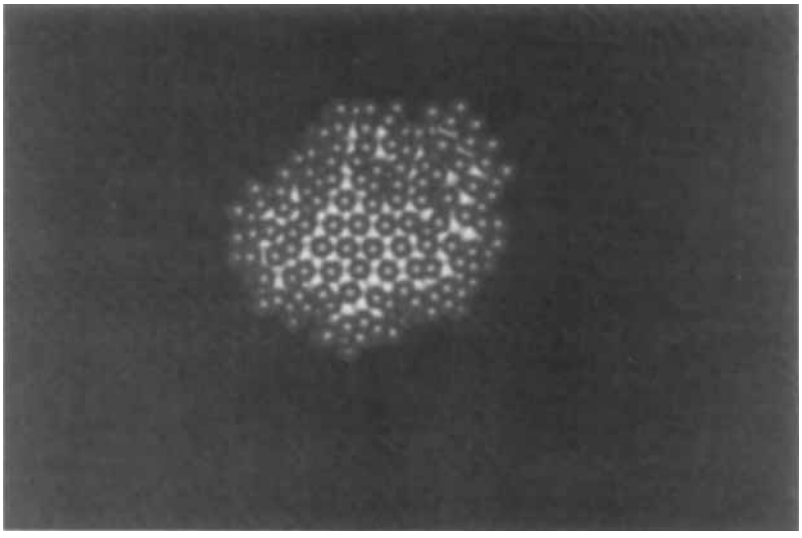

Figure 9(a): Photograph obtained using a computer graphical realization of the atoms comprising the underlying crystal (shown in red) and those in the first interfacial shell (shown in blue) for a single Molecular Dynamics snapshot during crystal growth. (see colour plates)

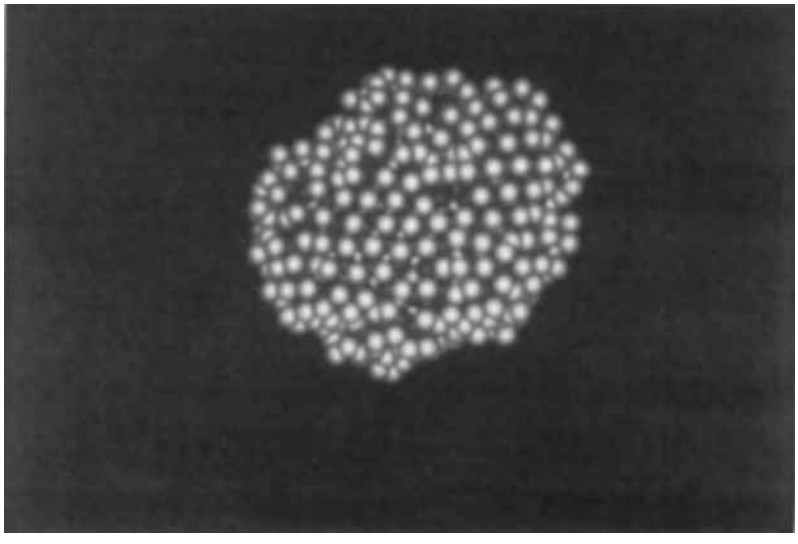

Figure 9(b): Photograph obtained using computer graphics of the positions of the atoms in the second interfacial shell (shown in yellow) relative to those in the first interfacial shell (blue) and the underlying crystal (red) for the same MD snapshot as in (a). The yellow atoms are either disordered or are located in HCP sites, not FCC ones. (see colour plates)

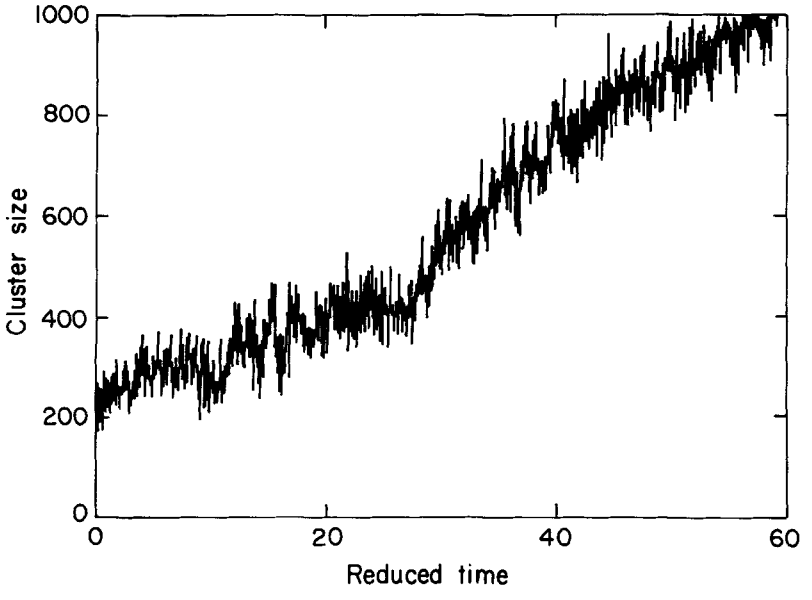

Figure 10 Growth of an implanted Lennard-Jones crystalline cluster as a function of reduced time. The initial size of the implanted cluster was 200 atoms. The temperature of the system is 0.45 in reduced units (about 70% of T_m).

5.3 *Results for the LJ system*

The angular criterion developed above was used to study crystal growth and dissolution processes at sub-T_m temperatures. The potential model used in these studies was the modified LJ potential used by Broughton and Gilmer [37] in their extensive studies of the solid/liquid interface. The reduced triple point temperature for this potential is known to occur at $T^* = 0.61$; note that this may be different from the melting point of the LJ potential used by Swope and Andersen [23].

Results were obtained for the crystal growth of an implanted seed crystal of 150 atoms in a liquid at zero pressure and a temperature, $T^* = 0.45$ (*i.e.* an undercooling of $\simeq 26\%$) using an MD simulation of 13,500 atoms in an NVE ensemble; see Figure 10. The parameters for F fitted at $T^* = 0.45$ were used for this simulation. The size of the implanted spherical seed was chosen to be close to the critical cluster size predicted by classical nucleation theory. The resulting kinetics of the growth process will be described in a subsequent paper, where the cluster size-time information generated by simulations, such as those described here, will be transformed into rate information.

6 SUMMARY

Criteria have been developed which allow the differentiation of atoms into two classifications (solid-like and liquid-like) in a heterogeneous system containing both

crystal and liquid. For the SW potential, the 3-Body and the Angular criterion both work well in identifying the extent of a growing solid cluster, starting from an implanted seed crystal of an appropriate size.

The growth of LJ crystals was followed using an angular criterion to distinguish the extent of the solid-like cluster in the system. While more subjective than the SW case, an adequate recognition of solid was found to be possible. This criterion was shown to be capable of following the time evolution of a growing LJ crystal. During the early stages of growth, a strong tendency to form (111) facets was found.

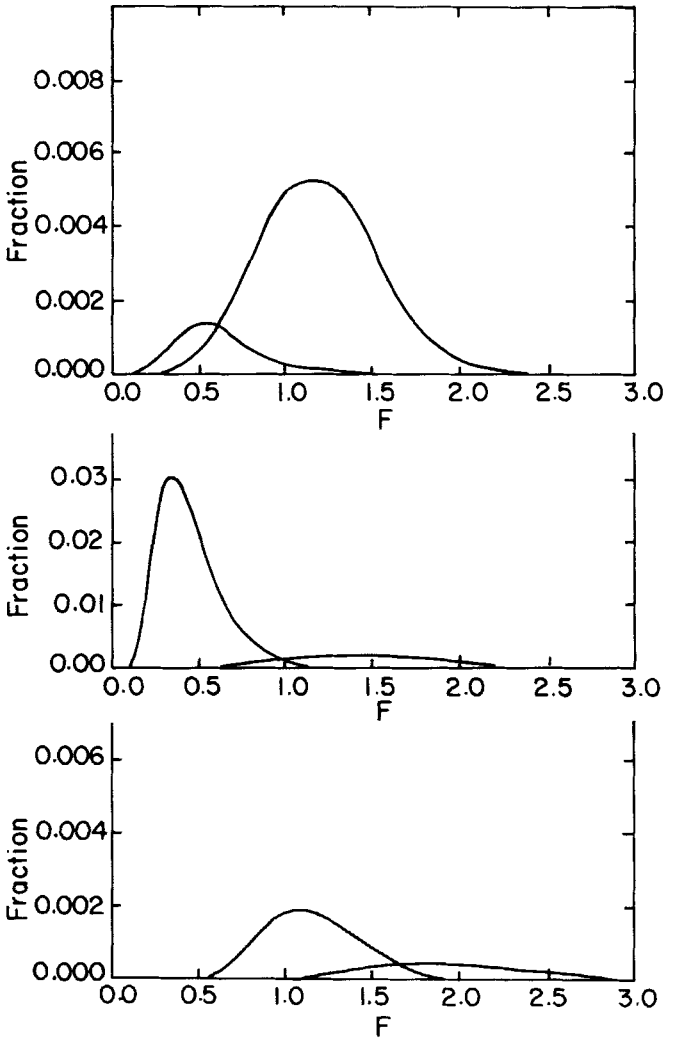

Figure 11 Distribution of the angular order parameter, F, for atoms with 11, 12 and 13 nearest neighbors, respectively, in the top, middle and bottom diagrams. The temperature of the system is 0.60 in reduced units.

The details of atomic attachment and detachment processes were found to be very similar for both the SW and LJ potentials, with considerable co-operative activity between tiny clusters of atoms. The dynamics of the growth process observed on the atomic level appear to be very complex and likely to elude representation by a simple physical model.

Acknowledgements

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APPENDIX A

During thermal vibrations, a particle may be located off its 0 K lattice position at the instant when the angles between the triplets of atoms are measured. In other words, an atom can be momentarily outside the maximum nearest neighbor distance, r_n, when F is calculated. In a complementary sense, an atom can be included as a nearest neighbor due to its transient 'straying' into a position close to other atoms. These 'accidental' omissions or inclusions of nearest neighbors increase at higher temperatures and can alter the value of F. To avoid these problems, we classify atoms as solid or liquid based on an F_C value that varies according to the number of its nearest neighbors. The values of F_C for atoms with 11, 12 and 13 neighbors were determined by collecting appropriate statistics; see Figure 11. Once the number of neighbors for a given atom was determined, the atom was classified as solid-like or liquid-like depending on its value of F relative to the appropriate value of F_C for its number of neighbors. Consideration of other numbers of neighbors was unimportant due to their rarity. This procedure is not necessary at lower temperatures (*e.g.* $T/T_m = 0.7$), but it is required at temperatures around and above the melting point (*e.g.* in crystal dissolution studies). This adjustment to the method significantly improved the recognition of solid. At $T^* = 0.60$, this 'fine tuned' criterion correctly recognized 94% of a bulk solid and confused 4% of a bulk liquid.

Once all atoms have been classified as being either solid-like or liquid-like based on their F value, a further 'filter' is applied to the classification of the atoms. This filter was necessary because we noticed that simulations of the liquid phase frequently showed individual atoms which were classified as solid due to a transient coincidence of the position of its neighbors. The reverse case (of isolated liquid atoms in a bulk solid) is also observed. The filter acts to eliminate these incorrectly-identified atoms in the following manner: If an atom had been designated as solid-like but had less than three solid-like neighbors, this atom was reassigned to the liquid phase. This value of 'three' was determined in the following way. The original code was used to determine how many atoms of a bulk liquid were wrongly identified as solid (i.e. no filter applied). Then this determination was repeated for

cases in which we reassigned solid-like atoms to the liquid phase if they had less than a certain number of solid-like neighbors. The results are shown in Table A2. A simulation in which atoms having less than three solid-like neighbors were reassigned to the liquid resulted in 12 atoms being confused as solid out of a total of 13500 atoms in the liquid system (*i.e.* less than 0.1%).

In a complementary sense, if an atom was classified as liquid-like but had more than eight solid-like neighbors then it was reassigned as solid. The value of 'eight' represents the maximum number of solid-like atoms that a liquid-like atom can have and still be considered as liquid-like. In a similar manner to that for the solid, this number was determined by considering a bulk solid system and observing how many atoms were confused as being liquid-like if the maximum number of solid-like neighbors was varied between 7 and 11; see Table A3.

The effect of this on a bulk phase is as follows: for a bulk crystalline phase at $T^* = 0.6$, the criteria used without the filter recognized 94% of the atoms as being solid. With the filter, essentially 100% of the atoms were correctly identified as being solid. Similar results were found for a bulk liquid. The effect of using the filter on a heterogeneous system of solid and liquid will be felt most strongly in the interfacial region and may change the size of the solid cluster identified in a heterogeneous solid/liquid system. It appears that the determination of the minimum number of solid-like atoms necessary to define a truly solid-like atom is the more important of the two parameters in this case. Use of the filter also reduced fluctuations in the cluster size as a function of time, greatly reducing the 'background' noise in the results. The filter was used throughout our subsequent investigations.

Finally, an analysis of the sensitivity of the cluster size recognized by this method was undertaken in which different parameters for the angular order parameter,

Table A2 Effect of applying the filter in a bulk liquid phase.

Minimum number of solid neighbors necessary to represent a solid atom	*No. of atoms confused as solid (from a system size of 13,500)*
No filter	478
1	234
2	56
3	12
4	0
5	0

Table A3 Effect of applying the filter to a bulk liquid phase.

Maximum-allowable number of solid neighbors for a liquid atom	*No. of atoms confused as solid (from a system size of 13,500)*
No filter	330
11	188
10	79
9	22
8	4
7	0

F_C, were used. If the values of F_C for 11, 12 and 13 neighbors were altered by $\pm 10\%$ simultaneously, the cluster size changed by roughly 10% (increasing in size as F increased: decreasing in size when F was decreased). The cluster size is also sensitive to the value of r_n used. If r_n is increased by 10%, the cluster size increased by 10%. If r_n is decreased by 10%, the cluster decreased by 50%! The uncertainty in the value of r_n which we chose is no more than 5% overall, and, due to the steepness of the first peak, the value of r_n is unlikely to be more than 1% smaller than the chosen value.

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[4] The algorithm is $O(n^4)$ in the number of candidate neighbors to a given atom. For a configuration where roughly 12 nearest neighbors are expected, the number of candidates can easily exceed 25. For lattices like the FCC, some refinements are necessary, e.g. averaging the position of the atoms over a certain interval and the removal of small edges of the Voronoi polyhedra.

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