An Introduction to Two Phase Molecular Dynamics Simulation

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I. Purpose of Document

The purpose of this document is to provide a practical introduction to the simulation of equilibrium two-phase molecular dynamics simulations. In its current state, the document examines two cases: vapor-liquid equilibrium and solid-liquid equilibrium.

II. Molecular Dynamics vs Monte Carlo

Monte Carlo (MC) simulations provide an elegant way to simulate two phases in equilibrium. Because in MC it is possible to run in the Grand Canonical ensemble, the chemical potential, μ, can be specified (and the number of atoms varies). Thus if one runs a liquid simulation at μ and temperature, T, and a vapor simulation at the same at μ and T, then those two simulations are by definition in thermodynamic equilibrium. There is no physical connection between the two simulated phases.

The advantage of the Molecular Dynamics approach is that the two phases can be simulated simultaneously. This provides the interface between the two phases. Since often times the important transport or reactive processes occur at the interface of the system, being able to simulate the interface holds great attraction.

III. Vapor-Liquid Equilibrium

Like any field, there is a history to the simulation of vapor-liquid equilibrium. In these brief notes, we do not recap the history of the pioneers in this field. Much of the content of this section is taken from the following references. This reference does contain, in the introduction, a recap of the available techniques and the justification for an alternative approach.

Authors: Fern, J.T., Keffer, D.J., Steele, W.V.
Title: "Measuring Coexisting Densities from a Two-Phase Molecular Dynamics Simulation by Voronoi Tessellations",
Journal: J. Phys. Chem. B. 111(13) pp. 3469-3475
Date: 2007
doi: 10.1021/jp0674470

Authors: Fern, J.T., Keffer, D.J., Steele, W.V.,
Title: "Vapor-Liquid Equilibrium, of Ethanol by Molecular Dynamics Simulation and Voronoi Tessellation",
Journal: J. Phys. Chem. B. 111(46) pp. 13278-13286
Date: 2007
doi: 10.1021/jp075414u

III.A. Initial Conditions

The goal of a two-phase molecular dynamics (2ϕMD) simulation is to simulate a statistically reliable amount of liquid and vapor phase. If one thinks back to our arguments for minimum system size there were two constraints. For dilute phases, there is a minimum number of particles (atoms or molecules) that should be simulated (often on the order of 100). Thus the vapor phase should occupy a sufficient volume to include 100 particles. For condensed phases, the constraint is that the size of the simulation volume should be at least twice the cut-off distance in the potential. The consequence of these two constraints is that one often ends up with non-square simulation volumes in which, $\ell_x = \ell_y << \ell_z$. This is because you need a large volume for the vapor phase but don't want a huge volume, which corresponds to a large number of particles, for the liquid phase. See, for example, Figure 1, in which the liquid phase is green and the vapor phase is blue. We will speak of the interface (red) later. In this figure, the number of vapor particles is kept above 100 and the *x* and *y* dimensions are set to something just larger than twice the cut-off distance. The total number of particles and the length in the *z* dimension are input in the simulation. They are chosen so that thickness in the liquid phase in the *z* dimension is greater than twice the cut-off distance. This requirement makes sure that the left interface and the right interface don't see each other through the potential. Of course, calculating this distance in the z dimension requires knowledge of the liquid and vapor densities. Since these are likely unknown at the start of the simulation, the determination of the initial aspect ratio and number of particles can be an iterative process. Of course, one can play it on the safe side and simulate larger than necessary systems so minimize the number of iterations. The 2ϕMD simulation is typically performed in the canonical NVT ensemble, in order to maintain the initial dimensions and aspect ratio of the simulation volume.

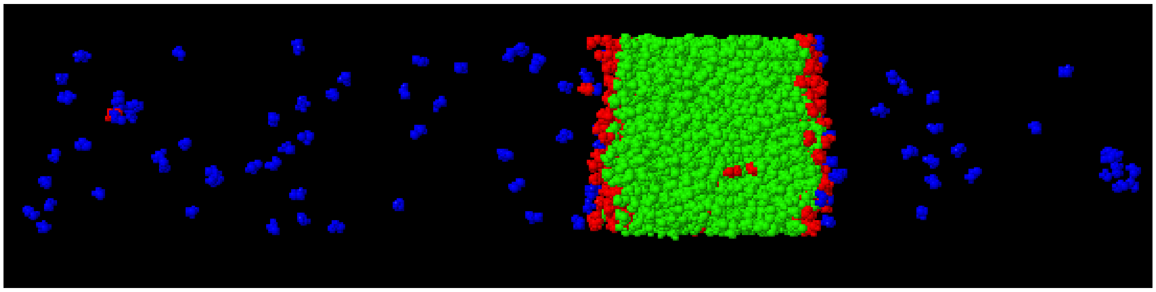

Figure 1. Screenshot taken from http://trace.lib.utk.edu/home/davidkeffer/sites/atoms/VLE/text/etoh_all.html. The liquid phase is green. The vapor phase is blue. The interface is red. This simulation is of ethanol at 375 K.

The initial positions of the particles are also important. If particles are placed randomly in the volume, you may not obtain a contiguous liquid phase but rather liquid droplets in the vapor phase. You will also not likely obtain a flat interface.

The simplest way to generate a reasonable initial configuration is to first simulate a pure liquid in a cubic simulation box. Those positions can be used as the initial positions of the liquid phase. Similarly a simulation of the pure vapor phase in a non-cubic simulation box corresponding to the remainder of the volume can provide the vapor particle positions. When these simulations are placed side by side, there may be overlap at the two interfaces. These are resolved either manually or through minimization.

Because the estimates of the liquid and vapor densities are approximate, depending upon how good the initial guesses were, some liquid particles may evaporate, becoming vapors, or some vapor particles may condense becoming liquid. If too much evaporation or condensation happens then you won't satisfy the system size constraints for both phases and a new initial condition will have to be generated based on these results.

III.B. Thermodynamic Properties

There are a variety of important properties one can obtain from 2ϕMD simulations. We categorize them here as thermodynamic and interfacial properties. The thermodynamic properties of greatest interest are often the liquid and vapor densities and the vapor pressure. Determining these quantities in the 2ϕMD simulation can be problematic because the physical bounds of the liquid and vapor phases are difficult to estimate and the formula for the pressure contains a long-range correction that assumes a spatially homogeneous system. Obviously, a system with two phases of varying density is not spatially homogeneous.

Therefore, various approaches have been implemented to obtain thermodynamic properties. We present one approach here that does not suffer from any arbitrary choice of the definition of liquid and vapor phase. This approach relies on Voronoi Tessellation. Voronoi tessellation allows one to divide (in this case a three-dimensional) volume into sub-volumes in which all points within a given volume are geometrically closer to a given point (the particle position lying within that subvolume) than to any other point (particles lying in other subvolumes.) This in essence provides the "atomic volume" or "molecular volume" associated with each particle. Taken as a whole, you have a distribution of Voronoi volumes. In Figure 2, we show a two-dimensional example of the Voronoi Tessellation applied to a periodic system.

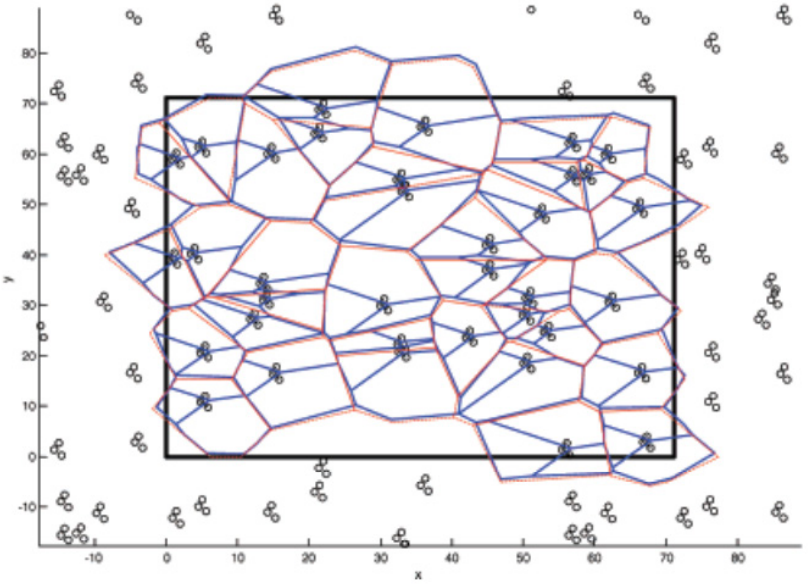

Figure 2. Voronoi Tessellation applied to a two-dimensional periodic system. In this example, the molecules are composed of three particles. The red lines correspond to the tessellation based on molecular center of mass. The blue lines correspond to the tessellation based on individual particles. For small molecules, the sum of the three particle volumes is very close to the molecule volume. [Fern et al., J. Phys. Chem. B, 2007 (b)].

The distribution of Voronoi volumes can be characterized by a mean, μ_V, and a standard deviation, σ_V. In order to determine the liquid and vapor phase molar volumes unambiguously, one can perform the following scheme.

1. Perform the 2φMD simulations.

2. Guess the mean Voronoi volume of each phase, μ_V^L and μ_V^V. Determine particles in each phase to obtain this mean. Compute standard deviation of Voronoi volume for the particles in each phase, σ_V^L and σ_V^V.

3. Perform 1φMD NVT simulations at those mean volumes, μ_V^L and μ_V^V. Compute σ_V^L and σ_V^V.

4.a. If the σ_V^L and σ_V^V from the 1φMD and 2φMD are the same within an acceptable tolerance, you are done.

4.b. If not, loop to Step 2 and make a new guess for μ_V^L and/or μ_V^V. Repeat until converged.

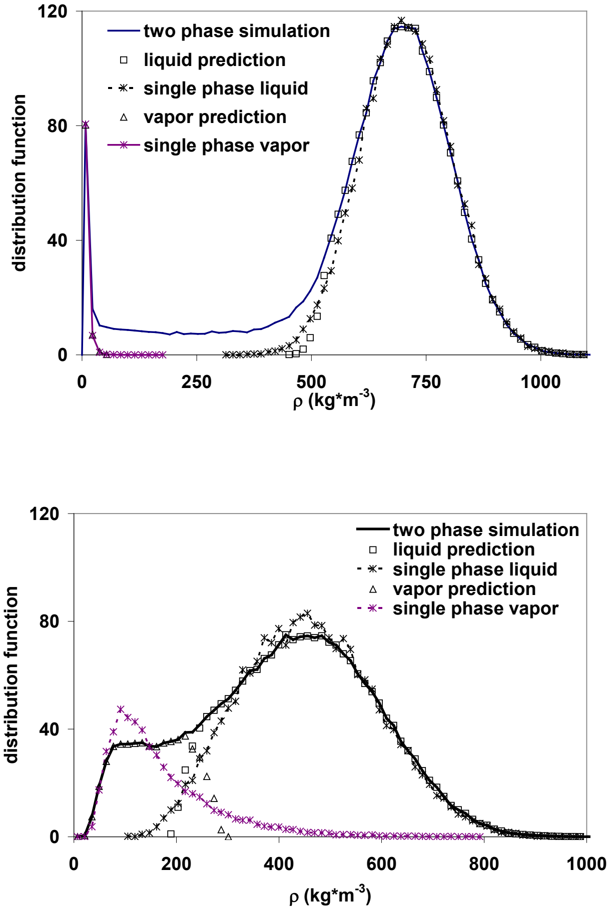

Figure 3. Distribution of Voronoi Volumes in 2φMD and 2φMD simulations of Lennard-Jones fluids at reduced temperatures of 1.0 (top) and 1.23 (bottom). [Fern et al., J. Phys. Chem. B, 2007 (a)].

In Figure 3, the final distributions of Voronoi Volumes using this approach are shown for a Lennard-Jones fluid at reduced temperatures of 1.0 (top) and 1.23 (bottom). The total Voronoi volume from the 2φMD simulation contains contributions from vapor, liquid and interfacial particles. The distributions from particles in the 2φMD deemed liquid or vapor are also shown and compared to the corresponding 1φMD simulations with the same μ_V^L and σ_V^L or μ_V^V and σ_V^V.

The liquid density comes directly from μ_V^L and the vapor density from μ_V^V. The vapor pressure was generated reliably in both the 1φMD simulations.

Interestingly, as seen in Figure 3, at low temperature, the interface is composed of particles that are neither liquid nor vapor. (That is some particles are not included in either the liquid or vapor Voronoi distribution.) However, at high temperature (approaching the critical point), the interface is composed of particles that are both liquid and vapor. (That is some particles are included in both the liquid and vapor Voronoi distributions.)

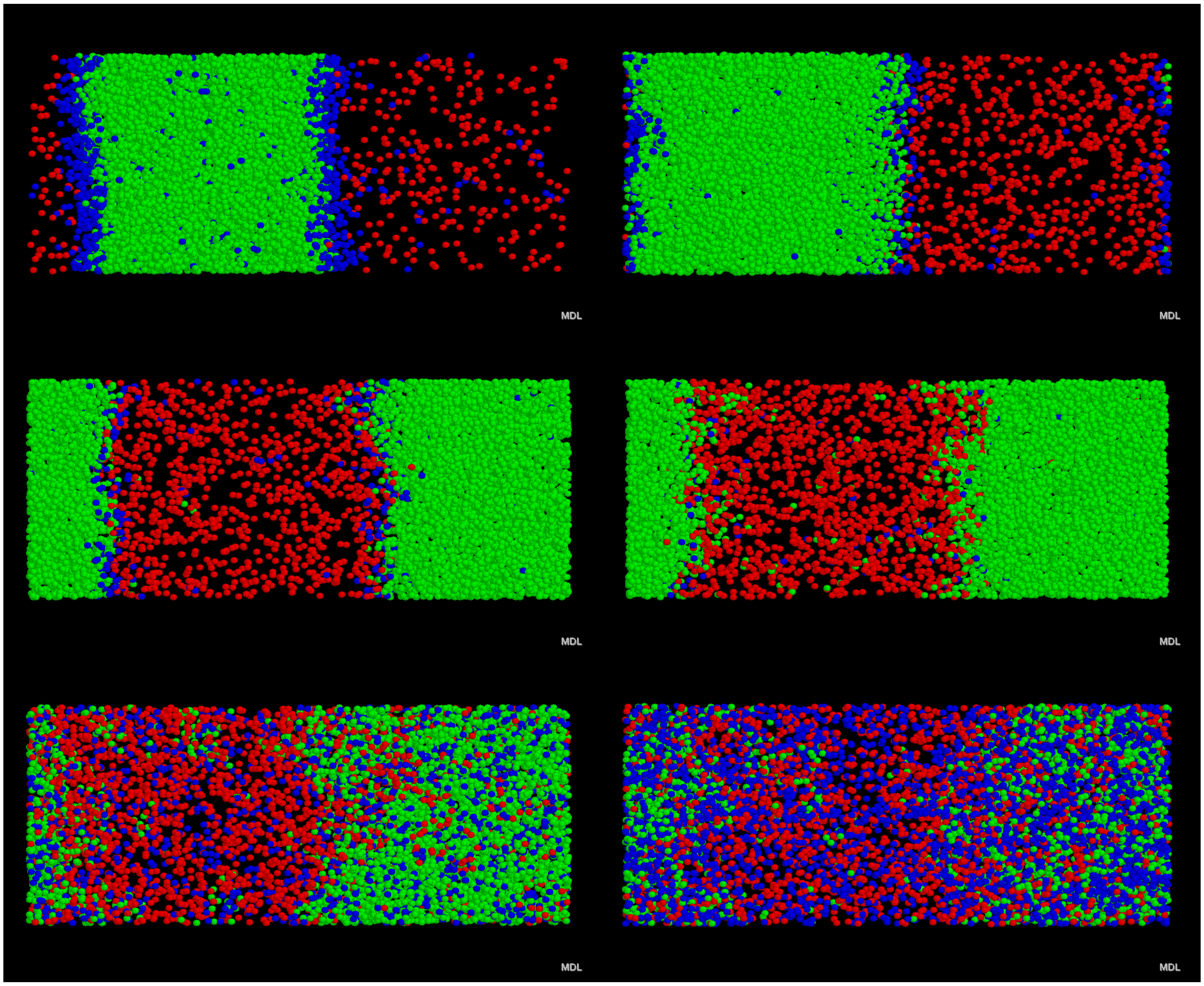

Figure 4. A snapshot of the final configuration for a reduced temperature of (a) 1.0, (b) 1.10, (c) 1.15, (d) 1.20, (e) 1.27, and (f) 1.29. In all plots, green represents the liquid molecules and red represents the vapor molecules. At the temperatures at and below 1.20 blue molecules are interfacial (neither liquid nor vapor) and at the high temperatures (above 1.20) blue molecules are both vapor and liquid. [Fern et al., J. Phys. Chem. B, 2007 (a)].

In Figure 4, at low temperatures, one clearly sees the liquid and vapor phases. As one approaches the critical temperature. The interface between liquid and vapor becomes diffuse before vanishing completely at the critical point. ($T_c = 1.293$)

In Figure 5, we show that the densities obtained from this process can be combined to create a phase diagram.

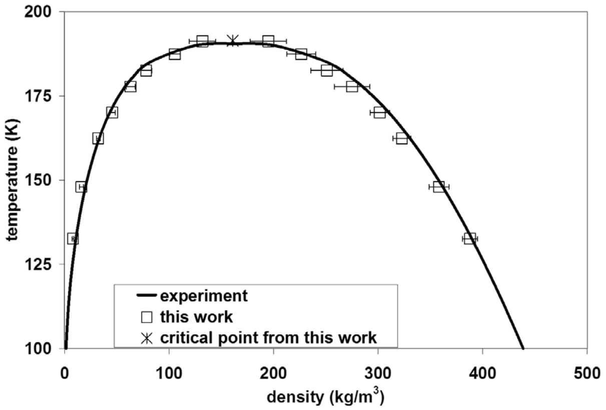

Figure 5. Phase diagram for methane from experiment and 2ϕMD simulation. [Fern et al., J. Phys. Chem. B, 2007 (a)].

III.C. Interfacial Properties

We noted that an advantage of 2ϕMD simulation is that the interface is present. This interface can be analyzed to give thermodynamic and structural properties. For a system with a planar interface, he surface tension can be evaluated based on the difference between the component of the pressure normal to the interface less that tangential to the interface, integrated from the liquid to the vapor phase. (In the single phase system, $p_N(z) = p_T(z)$.)

$$\gamma = \frac{1}{2}\int_{liquid}^{vapor}[p_N(z) - p_T(z)]dz \tag{1}$$

Thus equation (3) requires the simulation be divided into planar bins arranged parallel to the interface. The pressure computed based on the atoms in each bin. In Figure 6, we report the surface temperature of ethanol as a function of temperature. In Figure 7, the thickness of the interface is reported

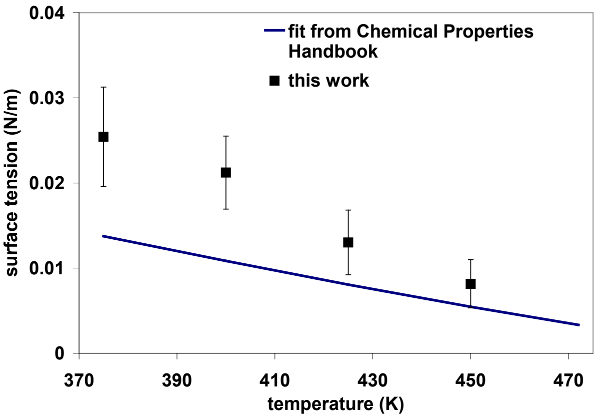

Figure 6: The surface tension (N/m) of ethanol as a function of temperature (K). The solid line is a fit from the Chemical Properties Handbook[39]. [Fern et al., J. Phys. Chem. B, 2007 (b)].

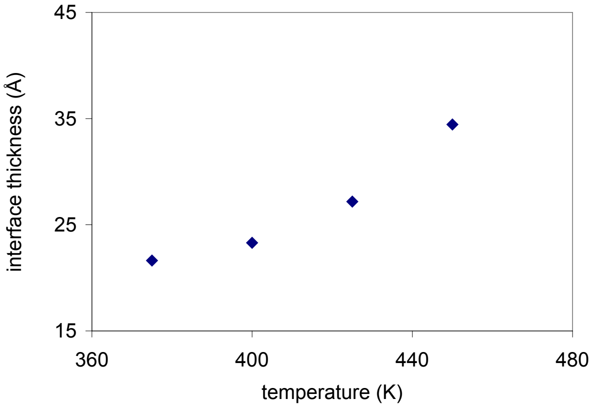

Figure 7: Interface thickness. [Fern et al., J. Phys. Chem. B, 2007 (b)].

The structure of the interface can also be studied. In Figure 8, the orientation of ethanol molecules at the interface is shown. As can be seen in Figure 8 there is a preferential orientation of the molecules at the interface. The range of the angle is 0° to 180° so that the average is 90° in an isotropic system. In the bulk liquid and bulk vapor, the average value of the orientation is indeed 90°. At each interface in our periodic system, there is deviation from the bulk value, corresponding to a systematic orientation of the ethanol molecule, such that the alcohol group is closest to the liquid droplet. This orientation maximizes the hydrogen bonding of the interfacial ethanol with the dense liquid phase. As temperature increases, we observe less orientation indicating that this preferential orientation is indeed energetic in nature.

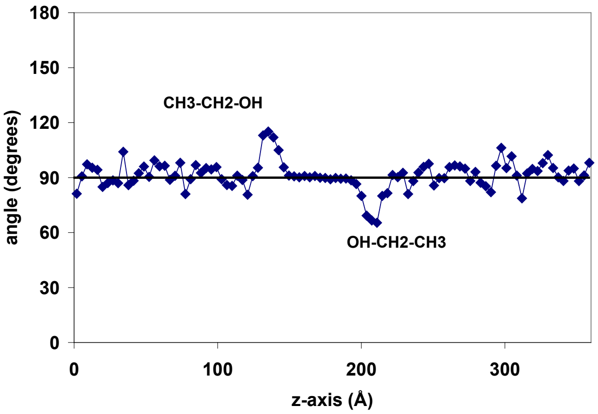

Figure 8: Spatial histogram of average molecular angle within the simulation cell at 375 K. [Fern et al., J. Phys. Chem. B, 2007 (b)].

IV. Solid-Liquid Equilibrium

Much of the content of this section is taken from the following reference.

Authors: J. R. Morris, C. Z. Wang, K. M. Ho, and C. T. Chan
Title: Melting line of aluminum from simulations of coexisting phases
Journal: PHYSICAL REVIEW B, VOLUME 49, NUMBER 51 pp. 3109-3104.
Date: FEBRUARY 1994

IV.A. Initial Conditions

As was the case for the vapor-liquid 2ϕMD simulation, the solid-liquid 2ϕMD simulation also requires a reasonable initial condition. In this case, part of the simulation volume is initially solid and another part liquid.

Also, as was the case above, the simulation volume is non-cubic. This allows the simulation of "bulk" liquid and solid without creating a tremendously large system.

IV.B. Thermodynamic, Interfacial and Dynamic Properties

From the analysis of 2ϕMD simulation, one can obtain a variety of properties. The first property is the melting temperature. If the temperature of the simulation is too high, the liquid volume will begin to crystallize. If the temperature of the simulation is too low, the solid volume will begin to melt. In Figure 9, we show three cases, for a low temperature, a temperature near the melting point, and a high temperature.

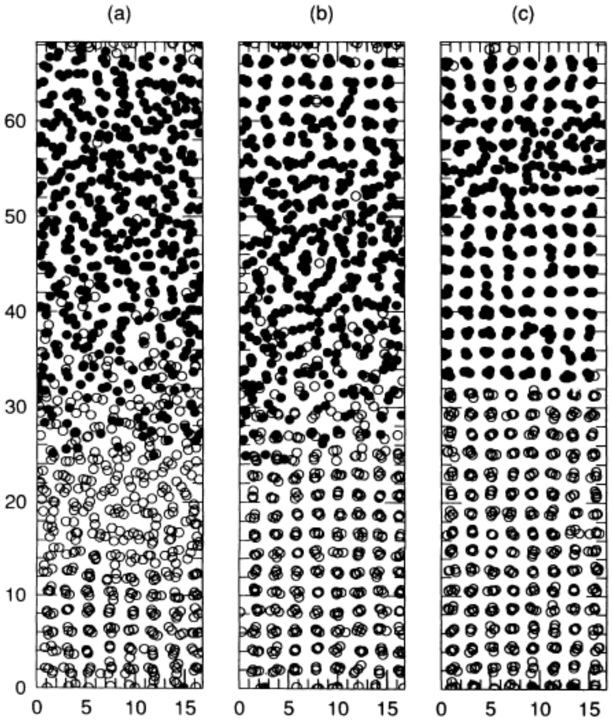

FIG. 1. Possible final configurations after equilibrating the system. The particle positions have been projected onto the x-z plane. Open circles indicate atoms that were initially in the solid phase; closed circles indicate atoms initially in the liquid phase. Distances in angstroms are indicated on the axes. (a) Example of a system that has almost completely melted. (b) System in which some of the solid phase has melted and some of the liquid phase has solidified. (c) System that has almost completely crystallized.

Figure 9. Possible final configurations as a function of temperature.