Phase diagram of carbon-oxygen plasma mixtures in white dwarf stars

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Abstract.

The liquid-solid phase-diagram of dense carbon-oxygen plasma mixtures found in white dwarf stars interiors is determined from molecular dynamics (MD) simulations. Our MD simulations consist of boxes with 55296 ions with different carbon to oxygen ratios. Finite size effects are estimated comparing the new MD simulations results to previous smaller simulations. We use bond angle metric to identify whether an ion is in the solid, liquid or interface and study non-equilibrium effects by obtaining the diffusion coefficients in the different phases. Our phase diagram agrees with predictions from Medin and Cumming obtained by an independent method.

1. Introduction

White Dwarf (WD) stars are planet sized remains of conventional stars that no longer burn nuclear fuel. The vast majority of WD stars have carbon and oxygen in their cores as they are the evolutionary end of stars not massive enough to synthesize heavier elements. Observations of the cooling curves of these stars provide important information on the evolution and age of a stellar population [1]. The core of a WD is a plasma of charged ions immersed in a degenerate electron gas. As the star cools by radiating away its internal heat this plasma crystallizes. This can delay the WD cooling [2]. Recently, Winget et al. observed effects from the latent heat of crystallization on the luminosity function of WDs in the globular cluster NGC 6397 [3]. These observations allow one to determine the melting temperature of the carbon and oxygen mixtures inside WD stars, which impose constraints on the ratio of carbon to oxygen in the core.

In this paper we determined from molecular dynamics (MD) simulations the melting temperature and other properties of the liquid-solid phase diagram for carbon-oxygen plasma mixtures. Phase diagrams for these mixtures have been calculated before assuming a local density model for the free energy of the solid [4] or based on Monte Carlo and MD simulations of free energies for both the liquid and the solid phases[5–8]. Recently Potekhin et al. have made accurate calculations of the free energy of liquid mixtures [9, 10] and Medin and Cumming calculated the phase diagram for both binary mixtures such as C/O and much more complicated multicomponent mixtures [11].

All of these works determine liquid-solid phase equilibria by equating liquid and solid free energies that have been calculated separately. This procedure allows the use of smaller Monte Carlo or MD simulations where only a single phase is present at a time. However, it may be
very sensitive to any small errors in the free energy difference between liquid and solid phases. Indeed for the C/O system, Segretain et al. [4] predict higher melting temperatures and a spindle type phase diagram while both Ogata et al. [5, 6] and Medin and Cumming [11] predict lower melting temperatures and an azeotrope type phase diagram. In a spindle-type phase diagram the melting temperature of the mixture is always greater than the melting temperature of pure carbon, while in an azeotrope type phase diagram the melting temperature of the mixture can be lower than that of pure carbon. This difference in phase diagrams could be due to small errors in Segretain’s solid free energies.

Furthermore, equating the free energies of liquid and solid phases provides no information on the dynamics of the phase transition nor are interface properties addressed. For multicomponent systems there is, in general, a gradient in composition across the liquid-solid interface. To our knowledge the spatial extent of this gradient has not been determined. Recently, we performed direct two phase molecular dynamics simulations of liquid-solid phase equilibria both for carbon/oxygen mixtures in WD [12] and for a complex 17 component mixture modeling the crust of an accreting neutron star [13]. These simulations have both liquid and solid phases present simultaneously which allows for a direct determination of the melting temperature, and the composition of the liquid and solid phases from a single simulation. One of the advantages of this method is that phase equilibria for very complicated systems can be simulated. However, direct simulations need to address potential systematic errors from finite size effects and from the lack of thermodynamic equilibration. Finite size effects are potentially important because one must fit not only liquid and solid phases but also two liquid-solid interfaces within the simulation volume. This, in general, requires a larger simulation volume than for simulations of only a single phase. Nevertheless, recent computer advances reduced dramatically the computational limitations on these larger simulations. It is now easy to simulate much larger systems than have typically been run in the past.

One must run these two-phase simulations long enough to ensure that the phases have come into thermodynamic equilibrium. This may require impurities to diffuse throughout the solid phase. However, diffusion in the solid phase is relatively fast, for these Coulomb systems, because the ions do not have hard core interactions. There is only a relatively soft $1/r$ interaction between ions. As a result, ions can move past one another. We have studied diffusion in Coulomb crystals in a recent paper [14]. If finite size and non-equilibrium effects are addressed, direct two phase simulations should yield accurate results. The systematic errors from two-phase simulations are likely very different from previous free energy calculations. Therefore, comparing the two methods provides an important check on both approaches.

In this paper we perform larger MD simulations of C/O mixtures with 55296 ions and compare them to the 27648 ions we used previously [12]. This allows us to study finite size effects. We discuss our MD formalism in section 2, including a method based on local order parameter [15] to determine whether ions are in the solid liquid or interface, present results in section 3 and conclude in section 4.

2. Formalism

In section 2.1 we describe the formalism used in our MD simulations. The formalism is essentially the same we used in a previous work on carbon oxygen mixtures in WD [12]. In section 2.2 we discuss the procedure used to determine whether a given ion is in a liquid or solid phase.

2.1. MD Formalism

In our simulations we address a system of ions, of two different species, and electrons. Since the system is under great pressure all ions are fully ionized and electrons form a degenerate Fermi gas. The electronic structure of this relativistic electron gas is very simple and, therefore, does not need to be directly computed in the simulation. Ions interact with each other via a long
ranged Coulomb interactions, screened by the electron background. The potential between two ions, labeled $i$ and $j$, is
\[ v_{ij}(r) = \frac{Z_i Z_j e^2}{r} e^{-r/\lambda}. \]  

$Z_i$ and $Z_j$ are the ion charges, $r$ is their separation and $\lambda$ is the Thomas-Fermi screening length. For cold relativistic electrons $\lambda^{-1} = 2\alpha^{1/2} k_F/\pi^{1/2}$ where $\alpha$ is the fine structure constant and $k_F$ the electron Fermi momentum, $k_F = (3\pi n_e)^{1/3}$. The electron density $n_e$ is equal to the ion charge density, $n_e = \langle Z \rangle n$ where $n$ is the ion density and $\langle Z \rangle$ the average ion charge. Our simulations are classical and the electron mass has been neglected in order to be consistent with our previous work. However, the electron mass is important at the lower densities in WD and this may change our results slightly [16]. In addition, quantum effects could play some role at high densities [17]. The simulations can be characterized by an average Coulomb parameter
\[ \Gamma = \frac{\langle Z^{5/3} \rangle e^2}{a_e T}. \]  

Above $\langle Z^{5/3} \rangle$ is an average over the ion charges, $T$ is the temperature and $a_e = (3/4\pi n_e)^{1/3}$ the electron sphere radius. Time can be measured in units of one over the plasma frequency $\omega_p$, which depends on the ion charge $Z$ and mass $M$. Long wavelength fluctuations in the charge density can undergo oscillations at the plasma frequency. A hydrodynamical plasma frequency $\bar{\omega}_p$ from the simple averages of $Z$ and $M$ was defined for mixtures,
\[ \bar{\omega}_p = \left[ \frac{4\pi e^2 \langle Z \rangle n_e}{\langle M \rangle} \right]^{1/2}. \]  

Choices for the average over composition in Eq. 3 are not unique. However, $\bar{\omega}_p$ is not expected to change significantly for different choices. All of our simulations are run for the same electron density of $n_e = 5.026 \times 10^{-3}$fm$^{-3}$. Since the pressure is dominated by the electronic contribution, constant electron density corresponds, approximately, to constant pressure. The density can be scaled to any desired value by also changing the temperature $T$ so that the value of $\Gamma$, see Eq. 2, remains the same.

2.2. Interface Finding

All of our MD simulations consist of two phases, a solid phase and a liquid phase. Though determining whether an ion is solid-like or liquid-like may be simple by a visual inspection, this determination is not straightforward numerically. Also, as the system evolves ions can diffuse from one phase to the other or simply melt/solidify. Since we want to keep track of this and obtain quantities such as the composition and volume of each phase we need a numerical approach. The phase of an entire system can be determined by computing the global order parameter $Q_l$ [18]. The phase of individual ions was determined using a prescription laid out in reference [15].

For each ion $i$, an ion $j$ is defined as its neighbors if it is within a given radius $r_{min} = 4a$, where $a = (3/4\pi n)^{1/3}$ is the ion sphere radius. The vectors $\hat{r}_{ij}$ joining neighbors are called bonds and their direction can be described by the angles $\theta_{ij}$ and $\phi_{ij}$ in the frame of ion $i$. The local structure around ion $i$ can be characterized using spherical harmonics $Y_{lm}(\theta_{ij}, \phi_{ij})$ by
\[ q_{lm}(i) = \frac{\sum_{j=1}^{N_b(i)} \alpha(r_{ij}) Y_{lm}(\theta_{ij}, \phi_{ij})}{\sum_{j=1}^{N_b(i)} \alpha(r_{ij})} \]  

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where $N_b(i)$ is the number of ions bonded with ion $i$ and we chose

$$\alpha(r_{ij}) = \left(\frac{r_{ij} - 4a}{2a}\right)^2$$

if $r < 4a$ and zero otherwise.

These local order parameters can be large in both the solid and the liquid. The order parameter with $l = 6$ was chosen since is the most sensitive to the bcc structure of the solid on our simulations. The global order parameter

$$Q_6 = \left[\frac{4\pi}{13} \sum_{m=-6}^{6} q_{6m}^* q_{6m}\right]^{1/2}, \text{ where } q_{6m} = \frac{1}{N} \sum_{n=1}^{N} \bar{q}_{6m}(i),$$

(5)

is large in the solid due to the fact that the $\bar{q}_{6m}(i)$ add up coherently. In the liquid, $\bar{q}_{6m}(i)$ add incoherently, so $Q_6$ is small. This coherence is exploited to determine local order.

For each $\bar{q}_{6m}(i)$ a normalization is applied,

$$\bar{q}_{6m}(i) = \frac{\bar{q}_{6m}(i)}{\left[\sum_{m=-6}^{6} |\bar{q}_{6m}(i)|^2\right]^{1/2}}$$

(6)

and a dot product of the vectors $q_6$ is defined for neighboring particles $i$ and $j$,

$$q_6(i) \cdot q_6(j) \equiv \sum_{m=-6}^{6} \bar{q}_{6m}(i) \bar{q}_{6m}^*(j).$$

(7)

Note that, by construction, $q_6(i) \cdot q_6(i) = 1$.

As in reference [15] we define two particles to be connected whenever $q_6(i) \cdot q_6(j) > 0.5$. Then, we define a threshold on the number of connections to determine if an ion is solid-like or liquid-like. On average an ion in our simulations has 62 neighbors. The threshold value used was 20 connections. Thus, an ion connected to more (less) than 20 neighbors is labeled as solid-like (liquid-like). This criterion is met for most of the ions within a given phase. However, due to diffusion and thermal fluctuations, ions in the solid (liquid) may temporarily be connected to less (more) than 20 neighbors and be incorrectly labeled. Thus, we add an extra step to our algorithm which also enables us to establish where the liquid-solid interface is. Deep in the solid, a vast majority of the ions are identified as solid-like. In the bulk of the liquid a similar majority is identified as liquid-like. Along the interface, there is a mixture of solid-like and liquid-like ions. For this reason, we tag an ion as being in the solid or liquid if a large majority ($> 0.80$) of ions within four lattice spacings are in the same phase. If this criterion is not met, then the ion is determined to be in the interface. Notice that ions determined to be in the interface are found where one would expect them (see figure 1), along the border of the solid and liquid phases.

3. Results

In this section we present our results for the evolution of three large MD simulations of liquid-solid systems. Each system had a different carbon to oxygen ratio and from their final compositions the phase diagram was obtained. Diffusion coefficients were estimated in order to monitor non-equilibrium effects.
The MD simulations consisted of boxes with 55296 ions which were twice as long in the $z$ direction as in the $x$ and $y$ directions. As in reference [12], we used periodic boundary conditions and the potential between ions was obtained from the single interaction between the nearest periodic image. Note that the rectangular geometry increases the distance between the two liquid-solid interfaces compared to cubical simulation volume. We expect this to minimize finite size effects. To decrease simulation time we used a cut-off distance $r_{\text{cut}} = 8\lambda$ when calculating the potential between ions. Taking the cut-off into account the potential between ions is altered to

$$v'_{ij}(r) = v_{ij}(r) - v_{ij}(r_{\text{cut}}).$$

This cut-off is large enough that the phase diagram should not be altered by it and, still, significantly smaller than the sides of the box so that Ewald sums over periodic images do not have to be included. We also point out that we do not include gravity in our simulations as the sides of the boxes are of the order of 1 000 fm while the radius of a white dwarf star is 19 orders of magnitude larger, about 10 000 km.

The initial conditions consisted of two cubes with 27648 ions, one in the liquid phase and one in the solid phase, stacked together along the $z$ direction. Throughout the paper, for convenience, we will refer to the top (bottom) of the box as the fraction of the box along the $z$ direction where the liquid (solid) cube was initially placed. We note here that this naming scheme was chosen arbitrarily since, because of periodic boundary conditions, the simulation volumes have no physical discernible top or bottom. Initial composition of each phase and temperature of the system was based on our results for previous simulations with cubic boxes [12].

### 3.1. The 75% oxygen run

The first simulation to be discussed had 75% oxygen and 25% carbon by number, or $x_O = 0.75$ and $x_C = 0.25$. Liquid and solid phases were prepared independently and then combined to form the initial 55296 ions system. Based on previous work suggesting that the solid will be enriched in oxygen we prepared the solid phase to be composed of 80% oxygen, $x'_O = 0.80$. Here $s$ denotes the solid phase. Since each volume contains half of the 55296 particles, the liquid phase was prepared enriched in carbon; $x'_lO = 0.70$, where $l$ denotes the liquid.

In order to obtain the 27648 crystal we started with a 3456 ion box. Ions were placed in the box with random positions and velocities and oxygen number fraction of $x'_O = 0.80$. The system was cooled until it crystallized and, then, 8 copies of the crystal were combined to form a 27648 system. This system was evolved for $\bar{\omega}_p t = 8900$ at a $\Gamma = 213.1$.

The liquid box was obtained in a similar way. We started from a 3456 ion box with random positions and velocities, but a oxygen fraction of $x_O = 0.70$. This system was evolved at the same $\Gamma$ for $\bar{\omega}_p t = 4400$. Because of the larger carbon fraction the system does not crystallize at the same $\Gamma$ as the solid. Then, 8 copies of the system were combined to form the 27648 liquid. This system was evolved for a further $\bar{\omega}_p t = 8900$ and then placed on top of the solid box to form the initial 55296 ion configuration.

This initial condition is not equilibrated for a few reasons to be discussed. First, by just placing the liquid box on top of the solid one the interface may acquire a very high energy: ions in the liquid and the solid may end up very close to each other. Also, we expect the composition gradient across the solid-liquid interface to be smooth. That is not the case when the boxes are just placed on top of each other. The solid may not be equilibrated as diffusion in the solid phase is slow and the crystallized system was only evolved for a short time. Finally, the composition of each phase and the equilibrium temperature may be wrong, we need to wait for the phases to interact for some in order for it to reach equilibrium.

The full system was evolved for a total time of $2.2 \times 10^6\bar{\omega}_p t$ using a velocity Verlet [19] algorithm with a time step of $0.177/\bar{\omega}_p$. During the run we rescaled the velocities every 100
time steps to keep the chosen temperature approximately constant. We also slowly adjusted the temperature to ensure the fractions of liquid and solid would stay approximately the same. Though this does not conserve energy during the run, our main goal in this paper was to minimize finite size effects by keeping the two liquid-solid interfaces as far from each other as possible. We employed a simple hybrid OpenMP/MPI computer code and used about 768 cores on the Cray XT5 system Kraken [20]. The total run time was about two weeks.

Using the VMD software [21] we show in figure 1 the projection along the $yz$ plane of the final configuration. On the left figure particles are colored based on whether they represent carbon or oxygen ions. The bottom half of the simulation volume is seen to contain a crystalline region. On the right figure we used the procedure of Sec. 2.2 to determine which parts of the system are liquid, solid, or belong to the two liquid-solid interfaces and colored particles accordingly. Note that the interface regions are not rectangular and show some fluctuations. These fluctuations were observed to change with time, even though the volume of the interface did not (see figure 2).

![Figure 1.](image)

In figure 2 we show the fluctuations in temperature

$$\delta \Gamma = \frac{\Gamma - \bar{\Gamma}}{\bar{\Gamma}}$$

where $\bar{\Gamma}$ is the average of $\Gamma$ over the last third of the run, see table 1. Initially the temperature had to be kept low (high $\Gamma$) in order to keep the non-equilibrated solid from melting. After a short time the system equilibrates and the fluctuations in temperature are only of the order of half of a percent.

Also shown in the same figure are the volume fractions of the solid and liquid phases and the interface. Note that the interface volume fraction barely changes over the total run. Its volume is mainly dependent on how we defined the interface, see algorithm described in section 2.2. Meanwhile, the total liquid and solid volumes fluctuate in about 10% of the total simulation.
Table 1. Equilibrium compositions of our 55296 ion runs. Oxygen number fraction of the whole system is $x_O$. Coulomb parameter averaged over the last third of the run $\bar{\Gamma}$ (determined from the final temperature and $x_O$). The composition of the solid is $x_s$, the liquid is $x_l$, and the interface regions is $x_i$. Statistical errors are quoted in the last digit in parentheses.

| $x_O$ | $\bar{\Gamma}$ | $x_s^O$ | $x_l^O$ | $x_i^O$ |
|-------|-----------------|---------|---------|---------|
| 0.75  | 203.9(6)        | 0.806(1)| 0.703(3)| 0.744(6)|
| 0.50  | 221.6(7)        | 0.552(1)| 0.454(3)| 0.494(8)|
| 0.25  | 213.3(6)        | 0.250(2)| 0.249(2)| 0.255(6)|

volume, even if their oxygen compositions (see figure 3) change only by 1%. In table 1 are also shown the average oxygen fractions of each phase for the last third of the run. We note that in this oxygen rich system the solid phase is enriched in oxygen, $x_s^O \approx 0.80$, the liquid phase becomes depleted in it, $x_l^O \approx 0.70$, and the interface has a value that is similar to the total oxygen fraction of the system, $x_i^O \approx 0.75$.

Figure 2. (Color on line) Fractional fluctuations in Coulomb parameter $\delta \Gamma$ (solid black line and right hand scale), see equation 9, vs simulation time in units of $10^6 \bar{\omega}_p t$ for a 55296 ion system with $x_O = 0.75$. Also shown are the fraction of the system that is solid (red squares), liquid (blue circles) or interface (brown triangles).

Figure 3. (Color on line) Number fraction of oxygen for solid (red squares), liquid (blue circles) or interface (brown triangles) vs simulation time in units of $10^6 \bar{\omega}_p t$ for a 55296 ion system with $x_O = 0.75$.

In figure 4 we show different quantities as a function of the height $z$ in the simulation volume averaged over the last one third of the run. We divided the simulation volume into fifty slices along the $z$ coordinate, with slice 1 being at the bottom of figure 1 and slice 50 being at the top. We show how (from top to bottom) the diffusion coefficients, oxygen number fraction and phase fraction change as a function of the height in the box. It is easy to see that slices that are mainly solid, 6 through 21, have higher oxygen fraction than the slices that are mainly liquid, slices 30 to 48. Also important to note is the composition gradient across both interfaces and the fact that composition in the liquid is much more uniform than in the solid. The later is due to the fact that the liquid equilibrates faster than the solid. This happens because ions diffuse much faster in the liquid, as discussed next.

Diffusion coefficients were calculated using the method discussed in [14] in order to check on
equilibration. The coefficients plotted in figure 4 have been normalized to a reference value

$$D_0 = \frac{3\omega_p a^2}{\Gamma^{4/3}}$$  \hspace{1cm} (10)$$

for both carbon and oxygen ions along the box, see also table 2. Diffusion for carbon in the liquid, $D^C$ is slightly larger than the for oxygen, $D^O$. This agrees with the result obtained in reference [22]. In the solid, as expected, diffusion is much slower than in the liquid, with $D^s_C$ being more than 70 times smaller than $D^l_C$. This result is similar to the diffusion determined for one component solids near the melting temperature in [14]. Moreover, in the solid $D^s_O$ is much smaller than $D^s_C$. Therefore, we expect the equilibration time of the system to depend more on $D^s_C$ than on $D^s_O$. This is because the system will equilibrate by having carbon ions diffuse out of the the solid to increase $x^s_O$ or into it to increase $x^s_O$.

**Figure 4.** (Color on line) Diffusion, oxygen fraction and phase fractions for the 55296 ion simulation that is 75% oxygen and 25% carbon as a function of the height $z$ of the simulation volume. Slices 0 and 50 contain the same data. Top: Diffusion coefficients for carbon $D^C$ (open squares) and oxygen $D^O$ (closed squares) as a function of the height of the box. Center: Oxygen number fraction as a function of the height in the box. Bottom: Fraction of ions in a given slice that are in the liquid region (blue circles), solid (red squares) and interface (brown triangles).

**Table 2.** Diffusion coefficients of liquid and solid phases averaged over the last third of the runs. Results are expressed as $D^p_X$ in units of $D_0$, see equation 10. The letter $p$ denotes the phase, $s$ for solid and $l$ for liquid, while $X$ stands for ion species, $C$ for carbon and $O$ for oxygen. Statistical errors are quoted in the last digit in parentheses.

| $x_O$ | $D^l_C$ | $D^l_O$ | $D^s_C$ | $D^s_O$ |
|-------|---------|---------|---------|---------|
| 0.75  | 0.80    | 0.65    | 0.011(1)| 0.0018(1)|
| 0.50  | 0.68    | 0.55    | 0.0074(4)| 0.0013(1) |
| 0.25  | 0.64    | 0.52    | 0.0032(3)| 0.0007(1) |
3.2. The 50% oxygen run
In this section we discuss the 55296 ion run with 50% oxygen and 50% carbon. This run was prepared much in the same way as the previous one, with the exception that now the solid was initially prepared to contain 55% oxygen and the liquid 45%. These compositions were also chosen based on our previous 27648 simulations [12].

We show in figure 5 the fluctuations in temperature $\delta \Gamma$ and the volume fractions of each phase as a function of simulation time. The evolution of the composition of each phase is shown in figure 6. The time dependence of the oxygen fraction in each phase is small. This suggests that the starting composition is very close to the desired equilibrium composition or that equilibrium is reached very slowly. Longer runs and runs starting from different initial conditions should be able to settle this.

![Figure 5](image)
![Figure 6](image)

Figure 5. (Color on line) Fractional fluctuations in Coulomb parameter $\delta \Gamma$ (solid black line and right hand scale), see equation 9, vs simulation time in units of $10^6 \bar{\omega}_p t$ for a 55296 ion system with $x_O = 0.50$. Also shown are the fraction of the system that is solid (red squares), liquid (blue circles) or interface (brown triangles).

Figure 6. (Color on line) Number fraction of oxygen for solid (red squares), liquid (blue circles) or interface (brown triangles) vs simulation time in units of $10^6 \bar{\omega}_p t$ for a 55296 ion system with $x_O = 0.50$.

In figure 7 we show the diffusion coefficients, oxygen number fraction and the fraction of each phase as a function of the height $z$ in the box. The qualitative discussion above for the 75% oxygen run is also valid for the 50% oxygen run. Diffusion in the liquid is much faster than in the solid and there are large fluctuations in the solid composition. The average composition for each phase in this run is quoted in table 1 while diffusion coefficients were quoted in table 2.

3.3. The 25% oxygen run
In this section we discuss the 55296 ion run with 25% oxygen and 75% carbon. This run was prepared much in the same way as the previous ones, with the exception that now both solid and liquid were initially prepared to contain 25% oxygen. This is because on our previous 27648 simulations the chemical separation between these two phases was shown to be small [12].

Figure 8 shows the fluctuations in temperature $\delta \Gamma$ and the volume fractions of each phase as a function of simulation time. As in the previous simulations the interface volume is approximately constant and the temperature fluctuations are within half of a percent of the average temperature for the last third of the run. The evolution of the composition of each phase is shown in figure 9. Unlike the richer oxygen systems, the solid phase is not enriched in oxygen, see table 1. The oxygen composition of the liquid and solid phases fluctuate less than one percent, figure 9, even if the total fraction of these phases fluctuate in about 20% of the total simulation volume, figure
8. The interface composition undergoes larger oscillations and is slightly oxygen enriched with respect to the solid and liquid phases. In the thermodynamic limit, which is the one relevant for the phase diagram, the interface composition is not relevant. However, the simulation might be showing a real effect where solid and liquid have very similar compositions and the interface is slightly oxygen rich.

In figure 10 we show the diffusion coefficients, oxygen number fraction and the fraction of each phase as a function of the height $z$ in the box. Again diffusion in the liquid is much faster than in the solid and there are large fluctuations in the solid composition. The interface again is only about 10% of the simulation volume, however looking at the bottom plot in figure 10 it seems that it stretches for a larger volume. This may be the case if the fluctuations in the interface are larger for this run than the other two. The average composition for each phase in this run is quoted in table 1 while diffusion coefficients were quoted in table 2.

### 3.4. The carbon oxygen phase diagram

This section discussed the phase diagram obtained from the compositions of the runs discussed in sections 3.1, 3.2 and 3.3. Figure 11 shows the phase diagram as a function of the oxygen composition. For historical reasons, the vertical axis is shown as the temperature divided by the melting temperature of pure carbon, assumed to happen at $\Gamma = 178.4$ \cite{12}. This temperature is slightly different than the one obtained for one component plasmas because we include the effect of electron screening.

The points plotted in figure 11 are the ones shown in table 1. In the same figure we plot the points obtained for 27648 ion simulations \cite{12}. When comparing the points of the two simulations we notice a few differences.

First, for the 55296 ion 25% oxygen simulation the composition of the liquid and solid phases seem to be about the same, whether in our previous run the solid seem to be somewhat enriched in oxygen. In addition, the equilibrium temperature for the larger system is slightly larger
**Figure 8.** (Color on line) Fractional fluctuations in Coulomb parameter $\delta \Gamma$ (solid black line and right hand scale), see equation 9, vs simulation time in units of $10^6 \bar{\omega}_p t$ for a 55296 ion system with $x_O = 0.25$. Also shown are the fraction of the system that is solid (red squares), liquid (blue circles) or interface (brown triangles).

**Figure 9.** (Color on line) Number fraction of oxygen for solid (red squares), liquid (blue circles) or interface (brown triangles) vs simulation time in units of $10^6 \bar{\omega}_p t$ for a 55296 ion system with $x_O = 0.25$.

**Figure 10.** (Color on line) Diffusion, oxygen fraction and phase fractions for the 55296 ion simulation that is 25% oxygen and 75% carbon as a function of the height $z$ of the simulation volume. Slices 0 and 50 contain the same data. Top: Diffusion coefficients for carbon $D_C$ (open squares) and oxygen $D_O$ (closed squares) as a function of the height of the box. Center: Oxygen number fraction as a function of the height in the box. Bottom: Fraction of ions in a given slice that are in the liquid region (blue circles), solid (red squares) and interface (brown triangles).

for the 55296 ion simulation. The 50% oxygen simulation with 55296 ions seem to have a larger difference in solid and liquid composition than the 27648 ion simulation, though almost the same equilibrium temperature. Finally, the 75% oxygen simulation with 55296 ions has a slightly higher melting temperature than the 27648 ion one. The differences between the 55296 and 27648 ion simulations suggest that there are some finite size effects playing a role in these runs. However, the differences are small enough that we can conclude that finite size effects are
Figure 11. (Color on line) Phase diagram for carbon-oxygen plasma mixtures. The horizontal axis represents the oxygen fraction $x_O$ while the vertical one represents the temperature scaled to a pure carbon plasma melting temperature, $\Gamma = 178.4$. The composition of the liquid phase (upper dashed red curve or red circles) that is in equilibrium with the solid phase (lower solid blue curve or squares). Our present results from 55296 ion simulations are filled symbols while the open symbols are our previous results with 27648 ions from reference [12]. The curves are the results of Medin and Cumming [11].

Alongside our MD simulation results in figure 11 are the curves obtained by Medin and Cumming [11]. The agreement between their model and our simulations is excellent. All three liquid points and two of the three solid compositions from table 1 are very close to Medin and Cumming’s results. There is a small difference in the solid composition of the 75% oxygen simulation. This difference could be due to small systematic errors in our simulations, our system still not being in equilibrium, or on small errors in the model of liquid and solid mixtures free energies used by Medin and Cumming. In any case, the small finite size corrections in going from a 27648 ion to a 55296 ion simulation improved the agreement between our results and Medin and Cumming’s. This suggests that the remaining errors due to finite-size and non-equilibrium effects in our direct MD simulation are small. It also suggests that the model free energies employed by Medin and Cumming are good, at least for carbon-oxygen systems.

We stress here that finite size and non-equilibrium effects might still be playing a role in the final result. Although small, finite size effects seem to have different effects on all three runs. First, the 25% oxygen run has a lower melting temperature and smaller composition difference between the liquid and solid phases. These points are in a region of the phase diagram where melting temperature, according to the model of Medin and Cumming, is almost independent of composition. Because of that, small errors may drastically change the composition of each phase.

For the 50% oxygen run the main difference is the larger composition difference between liquid and solid phases. This may arise if the gradient in the composition across the interface stretches over a distance comparable to the total size of the box. Because of that for the 27648 ion simulation the two interfaces may get significantly close to each other and the liquid and solid may end up with similar compositions.
There could also be a statistical component to the errors coming from a variety of non-equilibrium effects. For example, fluctuations in the location of an interface could create a new solid region and the composition of this region might not have time to equilibrate. Alternatively, there could be composition changes from large fluctuations. One could test for a variety of errors of this type by simply repeating these simulations a number of times with different initial conditions. Unfortunately, we have not had time to do this for the present paper.

We found that direct two-phase MD simulations can accurately determine liquid-solid phase equilibria. This result is very useful because direct MD simulation can be applied to many other systems, including very complex ones. Furthermore, direct MD simulations for a few compositions may provide very helpful benchmarks for simpler models. Note that simulations with a somewhat large number of particles may be necessary and these may have to be run for extended simulation times. However, rapid advances in computer power should make such simulations even easier in the future.

4. Summary and conclusions
The liquid-solid phase diagram for carbon-oxygen plasma mixtures using two-phase MD simulations was determined. Liquid, solid, and interface regions were identified in our simulations using a bond angle metric described in section 2.2. To study finite size effects, we performed 55296 ion simulations and compared to earlier 27648 ion results. To help monitor non-equilibrium effects, we calculated diffusion coefficients. We find that oxygen ions in the solid diffuse much slower than carbon ions and that both diffusion constants are 80 or more times smaller than diffusion constants in the liquid phase. There is excellent agreement between our phase diagram and that predicted by Medin and Cumming [11]. This suggests that errors from finite size and non-equilibrium effects are small, and that the carbon-oxygen phase diagram is now accurately known. This improved phase diagram can be used to explore the the evolution of cool white dwarfs, as done in [23]. In future work we will present phase diagrams for the three component carbon-oxygen-neon system and for the two component oxygen-selenium system. The oxygen-selenium system, with a larger ratio of charges than carbon-oxygen, can serve as a simple two component model of the complex rapid proton capture ash composition on an accreting neutron star [13].

Acknowledgments
We thank Z. Medin for helpful discussions. This research was supported in part by DOE grant DE-FG02-87ER40365 and by the National Science Foundation through TeraGrid resources provided by the National Institute for Computational Sciences under grant TG-AST100014.

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