Ab initio and classical Molecular Dynamics calculations of the high-pressure melting of Ne

L. Kočič, R. Ahuja1, 2, A. B. Belonoshko2, 3
1Condensed Matter Theory Group, Physics Department, Uppsala University, Box 530, S-751 21, Uppsala, Sweden
2Applied Materials Physics, Department of Materials Science and Engineering, The Royal Institute of Technology, S-100 44 Stockholm, Sweden
3Condensed Matter Theory, Alba Nova University Center, Physics Department, The Royal Institute of Technology, S-100 44 Stockholm, Sweden
E-mail: love.koci@fysik.uu.se

Abstract. Classical molecular dynamics (CMD) calculations are fast but are heavily dependent on the potential feasibility. On the other hand, first-principles (ab initio) molecular dynamics (AIMD) does not use any empirical knowledge, but can be extremely time consuming. As both techniques have been applied to study melting at extreme conditions, a comparison of the methods is motivated. Furthermore, when melting is studied with MD, the use of coexistent solid and liquid structures (two-phase) in the initial simulation configuration, instead of a only solid structure (one-phase), can have a significant impact. In this work, comparisons have been made between CMD and AIMD methods applied to one- and two-phase systems for the melting of Ne at high pressure.

1. Introduction
First-principles (ab initio) MD (AIMD) is based on the density functional theory (DFT) and the foundation of this theory was developed during the 1960’s. [1] Today, the application of ab initio methods are common in material studies. [2, 3, 4, 5, 6] Although numerical algorithms and the increasing performance of computer systems continuously are improving, ab initio calculations are still computationally expensive. Classical MD (CMD), on the other hand, is much faster and can treat millions of atoms. This is due to the use of empirical interatomic potentials where electronic effects are incorporated implicitly. However, it can be problematic to develop potential parameters that accurately describe the physical properties of the material studied. As no a priori potential is used in AIMD, possible sources to uncertainties by the potential choice and the parameter fitting can be avoided.

In this work, the high-pressure melting of Ne has been studied by classical and ab initio methods. Furthermore, comparisons have been made between homogeneous and heterogeneous melting: when the melting initiates with a liquid nucleation in the bulk, spreading throughout the solid structure, the transition is said to be homogeneous. Heterogeneous melting, on the other hand, begins at the surfaces, where atoms start to diffuse. Homogeneous melting can show big hysteresis effects, as a crystal can be superheated considerably above (and undercooled below) the equilibrium melt temperature ($T_m$). In MD, homogeneous melting can be resembled by the
heating of a crystal whereas heterogeneous melting can be modeled by the use of coexisting solid and liquid structures in the simulation box.

2. Models and technical details
The Lennard-Jones (L-J) potential,

\[ \Phi(r) = 4\epsilon \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6}, \]

has shown to reproduce thermodynamic properties of gases such as argon, [7, 8] xenon, [9] and krypton. [10] Here, we have examined the potential parameters for Ne with \( \epsilon/k = 35.1 \) K (\( k \) is the Boltzmann constant) and \( \sigma = 2.72 \) Å from Bellisent-Funel et al. [11] The L-J potential is implemented in the Moldy package [12] which was used for the simulations. Periodic boundary conditions (PBC) were applied to all six surfaces of the simulation box. One advantage when using PBC is the absence of surface effects, with the consequence that the melting of a one-phase system is homogeneous. In the calculations, the size of the time steps \( dt \) was set to 0.5 fs and the radius of the cutoff was 6 Å. A strict cutoff was applied, meaning that all interactions between pairs of sites within the radius were included.

The ab initio DFT calculations in this work were performed using the Vienna Ab Initio Simulation Package (VASP) [13, 14] in the NVT ensemble. Ultrasoft pseudopotentials were used to represent the ionic cores. The local-density approximation (LDA) was chosen as exchange correlation function, as it has been reported to perform well when calculating the ground-state properties of other noble gases as e.g. Xe. [15] The cutoff energy was 450 eV and the size of the time step was 0.5 fs. In conjunction with other recent studies, only the \( \Gamma \) point was used for the Brillouin zone integrations to avoid too long simulation times. [16, 17]

3. Results
By the use of a link cell method, [18] the CMD calculations in this work scale \( O(N) \) whereas the ab initio calculations performed with the VASP package scale \( O(N^3) \). Shown in table 1 are the CPU times for the first 10 MD steps for Ne when using AIMD or CMD. As there is a significant system size difference when comparing similar calculation times for the two methods, the purpose of the table is to emphasize the AIMD cost and the CMD efficiency.

### Table 1. CPU times for the 10 first steps in a MD calculation as a function of method, processors and atoms.

| Method | \( \# \) processors | \( \# \) atoms | CPU time (s) |
|--------|---------------------|----------------|-------------|
| AIMD   | 12                  | 2              | 1.5         |
|        | 4                   | 3.6            |             |
|        | 16                  | 37.7           |             |
|        | 32                  | 159.1          |             |
|        | 54                  | 507.2          |             |
|        | 108                 | 746.8          |             |
| CMD    | 1                   | 6912           | 1.1         |
|        | 16384               | 2.9            |             |
|        | 32000               | 5.6            |             |
|        | 108000              | 20.9           |             |
|        | 186624              | 36.6           |             |
|        | 500000              | 101.8          |             |
To initiate the setup for the two-phase simulations, two perfect fcc lattices containing 864 atoms each were constructed. One of these lattices, shown as 1) in Fig. 1, was simulated at a high temperature to transform into a molten configuration. The solid and molten structures were put together with a small spacing in a simulation box, letting the lower part of the box be solid and the upper part be liquid, as shown in 2). Starting from this configuration, the MD simulations result in a monophase. If the temperature is above the melting temperature $T_m$, the phase will become liquid (3a) whereas the phase will solidify if the temperature is below $T_m$ (3b). By narrowing the interval, the melting temperature can be estimated at the specific pressure in the simulation.

Belonoshko [19] and Tepper and Briels [20] have explained the two-phase simulation method in detail, and its successful application for a number of systems has been reported.[5, 21, 22, 23] For the rare gases in particular, the technique has recently been employed to study the melting of Xe. [24] Shown in Fig. 2 is the melting of Ne at high $PT$ conditions comparing different methods. The melting for the 1728 atom system (864+864, two-phase, NPT) and the 108 atom configuration (one-phase, NVT) with the L-J interaction from Bellissent-Funel et al. [11] were found by means of the radial distribution function. The simulations were performed for 40 000 and 3000 time steps, respectively. There is a discrepancy between the small and short one-phase runs and the big and long two-phase runs, as the former tend to overshoot the melting temperature. According to previous studies, [25, 26] this is expected. There is, however, another reason why to perform classical calculations of a small, one-phase system for a limited number of steps: a direct comparison can be made to the AIMD system, where these limitations often are necessary in order to avoid long computation times.

Compared to the results from the big two-phase system, there is also a melting temperature overshoot from the AIMD calculations. The CMD and AIMD melting results from this work are compared with one of the few predicted melting curves of neon at extreme conditions from Vos et al. [27] Clearly, there is a big discrepancy between this prediction and the AIMD one-phase...
calculations, as the latter need significantly higher temperatures to melt the crystal. However, this melting follows the one-phase L-J curve quite accurately. Although the two systems have been calculated with the same limitations, this results is highly interesting. This could also indicate the conformity between the AIMD and CMD two-phase calculations, where the melting accuracy of the previous method has been reported. [5, 21, 22, 23]

**Figure 2.** The melt line for the 1728 atom system (864+864, two-phase) with the L-J interaction from Bellisent-Funel et al. [11] was found by means of the radial distribution function. The simulations were performed for 40 000 time steps. Furthermore, the melt line from one-phase 108 atom simulations over 3000 time steps with the same potential is shown. The AIMD melting points were found from visual inspection of the atomic diffusion and the mean square displacement. The melting curve from Vos et al. [27] is also inserted.

4. **Discussion and conclusion**
Ahuja et al. [25] have reported the risk of overheating one-phase simulations in MD to find the melting temperature. However, bigger two-phase AIMD calculations, where liquid and solid configurations are simulated together, are extremely time consuming. In this paper, we have investigated the melting at high pressure of Ne by the use of classical and *ab initio* methods. Also, by comparing one- and two-phase CMD calculations, we have shown that the melting temperatures found by the one-phase configurations are slightly overestimated due to overheating. Although the high-pressure Ne melting curve determined by AIMD one-phase simulations is high compared to previous classical predictions, [27] it is found close to the CMD one-phase results in this work. Therefore, considering the documented accuracy of the two-phase method, the true melting curve could be found closer to the CMD two-phase results.

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