A toy model for simulating nucleation and phase transitions

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Developing an understanding of phase transitions is key to both technological and scientific advancement. Within this work, we show that a simple Markov Chain Monte Carlo approach is sufficient to successfully model the liquid-solid phase transition of bulk hydrogen. The approach consists of a Lennard-Jones potential to model intermolecular forces in combination with a Metropolis-Hastings algorithm to allow for the evolution of time. Hydrogen particles are confined to a box in $\mathbb{R}^2$ with periodic boundary conditions to allow for approximation of the bulk. When cooling this system from 100 K to the limit of 0 K; nucleation appears at temperatures in correspondence to the molecular solid region within the phase space of hydrogen.

I. INTRODUCTION

Self-organization is a fundamental aspect of nature. Without it, there would be no phase diagrams in our beloved textbooks. Within a phase diagram there exist regions of self-organized forms of matter. These regions consist of identical matter, yet their properties immensely differ. Obtaining a better understanding of phase transitions is key to the further development of science and technology. In order to do so several numerical schemes have been developed [1–3] allowing for the simulation of phase transitions. Despite the sophistication of the state-of-the-art numerical schemes, some phase transitions are still a matter of scientific debate [4]. Sophisticated methods exist, yet a toy model is beneficial for the understanding of a non-domain specialist. Within this work we take a Markov Chain Monte Carlo approach to simulate the nucleation of hydrogen particles confined to a box. This allows for insights to be obtained regarding the temperature at which nucleation begins within our hydrogen toy model. hydrogen is a well-studied material [5, 6], and hence is a good fit to test our toy model with. This work focuses on the transition towards a molecular solid as shown in Figure 1.

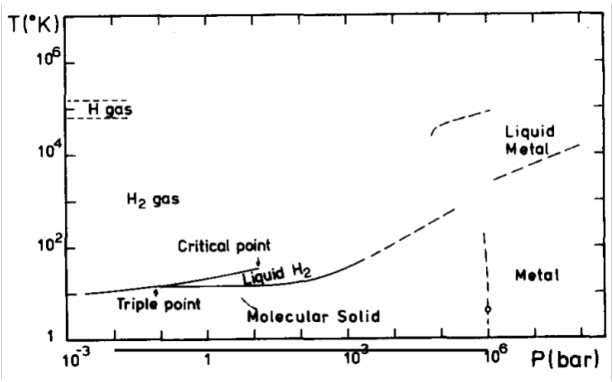

FIG. 1. A primitive phase diagram for hydrogen which used as a reference throughout this work. Figure source [5].

II. THEORY

We shall make the ansatz that the particles of interest consist of neutral circles in $\mathbb{R}^2$. This allows for intermolecular forces to be modelled by a truncated and shifted Lennard-Jones potential

$$u^{\mathrm{tr-sh}}(r_{ij}) = \begin{cases} u^{\mathrm{lj}}(r_{ij}) - u^{\mathrm{lj}}(r_c) & r_{ij} \leq r_c \\ 0 & r_{ij} > r_c. \end{cases} \tag{1}$$

Here r_{ij} denotes the distance between interacting particles i, j and r_c denotes the cutoff distance of the potential. The Lennard-Jones potential is given by

$$u^{\mathrm{lj}}(r_{ij}) = 4\epsilon\Big[\Big(\frac{\sigma}{r_{ij}}\Big)^{12} - \Big(\frac{\sigma}{r_{ij}}\Big)^{6}\Big]. \tag{2}$$

Where ϵ denotes the depth of the potential well and σ corresponds to the size of the particle. The Lennard-Jones parameters are depicted in Figure 2. Within this model the total potential energy of the system equals

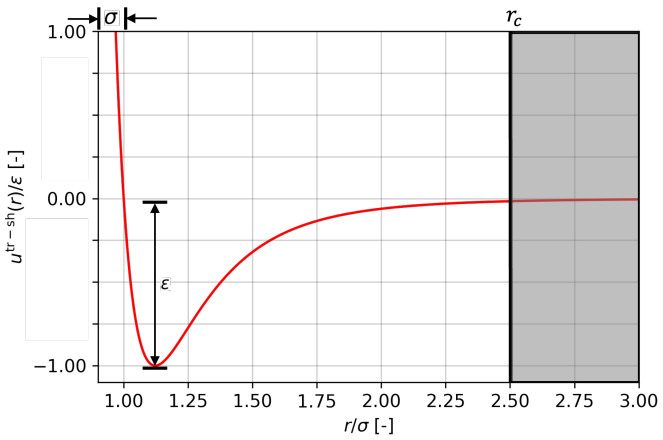

FIG. 2. The truncated and shifted Lennard-Jones potential with a visualisation of the particle size σ, the depth of the potential well ϵ and the cutoff distance r_c. The grey area emphasizes $u^{\mathrm{tr-sh}}(r \geq r_c) = 0$ for $r_c = 2.5\sigma$.

$$\mathcal{U}_{\text{tot}} = \sum_{i<j} u^{\text{tr-sh}}(r_{ij}) \tag{3}$$

where the summation runs over unique particle pairs.

In order to model the arrow of time, we minimize Equation 3 using a Metropolis-Hastings [7] Markov chain Monte Carlo approach as specified in Algorithm 1.

Algorithm 1 Pseudocode of the implementation of the Metropolis-Hastings algorithm. The uniform distribution $U \in [0, 1]$ is denoted as $U_{[0,1]}$.

1: **while** $T \geq 0$ **do**
2: Compute the potential energy $\mathcal{U}_{\text{tot}}(\vec{r})$.
3: Translate a random particle.
4: Compute the posterior potential energy $\mathcal{U}'_{\text{tot}}(\vec{r'})$.
5: **if** $\mathcal{U}'_{\text{tot}}(\vec{r'}) < \mathcal{U}_{\text{tot}}(\vec{r})$ **then**
6: Accept the step.
7: Decrease T.
8: Return to line 1.
9: **else**
10: Compute the probability of accepting this move p.
11: **if** $U_{[0,1]} \leq \min(1, p)$ **then**
12: Accept the step.
13: Decrease T.
14: **else**
15: Reject the step.
16: Return to line 3.

To elaborate on Algorithm 1; within this approach the system starts in some initial configuration $\vec{r}$. One particle i undergoes a random step towards $r'_i = r_i + \Delta$ with $\Delta \in U_{[0,\Delta_{\max}]}$. The decision of which particle i to move is made uniform at random. The probability of accepting the step $\vec{r} \to \vec{r'}$, if it does not lower the total potential energy, is given by

$$p = \exp\left(\frac{-(\mathcal{U}'_{\text{tot}}(\vec{r'}) - \mathcal{U}_{\text{tot}}(\vec{r}))}{k_B T}\right). \tag{4}$$

This ergodic Markov Chain allows for particle movement to be sampled according to the Boltzmann distribution [8].

III. METHODOLOGY

To simulate nucleation of hydrogen and investigate at which temperature nucleation starts, we simulate cooling of the bulk. This is done by modelling the evolution of a canonical ensemble within a square that has periodic boundary conditions. The location of the particles is initialised using Orthogonal Latin hypercube sampling [9]. This type of sampling ensures having an initial uniform particle density throughout the system. Our toy model consists of $N = 100$ hydrogen atoms with Lennard-Jones parameters $\sigma = 2.928$ $\mathring{A}$, $\epsilon = 3.138$ meV and $r_c = 2.5\sigma$. The hydrogen atoms are confined to a box of size 20σ by 20σ to allow for sufficient space for nucleation to appear at different sites. Within the numerical experiments, the system starts at a temperature of $T = 100$ K and is cooled towards the limit of $T = 0$ K in steps of $\Delta T = 10^{-3}$ K using an implementation of Algorithm 1 in Python. The computation of Equation 3 is distributed over all available CPU cores. However, considering the single-core speed of the Apple M1 chip, no further CPU time reduction techniques are implemented. The code is available at github.com/deKeijzer.

IV. RESULTS

To mitigate start-up effects of the Markov Chain the first few temperature evolutions are excluded from the analysis. Figure 3 displays the total potential energy versus the temperature of the system undergoing quasistatic cooling.

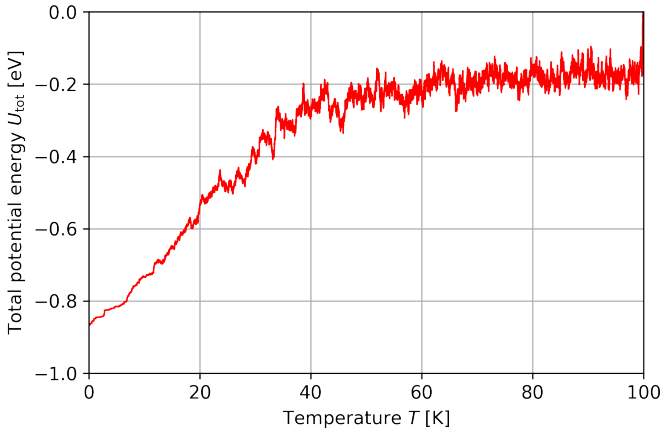

FIG. 3. The total Lennard-Jones potential energy of a system of 100 hydrogen particles as a function of temperature.

It is visible that for $T \gtrsim 40$ K the potential energy is asymptotic with stochastic noise visible along the energy axis. This noise likely occurs due to particles escaping from already paired groups. I.e. there is a temperature-dependent stochastic process visible where particles escape the energy well of the Lennard-Jones potential. Notice how the noise decreases with decreasing temperature. For temperatures $T \lesssim 40$ K we find that the potential energy decreases, it is this temperature range where nucleation starts. This is in agreement with the temperatures of the liquid-solid transition in Figure 1. We find that the implemented model exhibits aspects that are in agreement with previous [5] experimental and theoretical findings. To enlighten the phase transitions, configurations of the system at various temperatures are displayed in Figure 4. Nucleation is clearly visible; lattices including impurities appear for temperatures within the molecular solid region of hydrogen. Notice how some particle pairs have $||r_{ij}|| < \sigma$. This is explained by stochasticity, due to chance some particles within the bulk are non-ideally

close to one another. This shows that the system has not converged completely towards equilibrium conditions.

As an addendum, we tested our code with $N = 1000$ particles in a high-density system and find look-alike structures of the point charges on a circle [10] problem. This is displayed in Figure 5. Considering that groups of particles are not able to move in our model, nucleation appears at different locations throughout the system.

V. DISCUSSION

A Markov Chain Monte Carlo approach appears to be a feasible candidate in the study of the temperature dependence in the nucleation of hydrogen. The temperature at which nucleation starts coincides with previous findings within literature. In order to obtain more sophisticated insights methods of thermodynamic integration have to be implemented to e.g. obtain the pressure and density of the system. Having this information allows for the numerical creation of a phase diagram, after which theory and experiment are directly comparable. Moreover, considering the law of large numbers [11], numerical experiments with a larger number of particles have to be carried out in order to get probable results. This should be performed using proper stochastic simulation techniques, where a system of N particles is simulated M times whose averages $\langle\cdot\rangle_M$ are used to e.g. estimate the true density and pressure within the thermodynamic limit. Thus does require the need for more optimized numerical schemes in order to keep computation time reasonable.

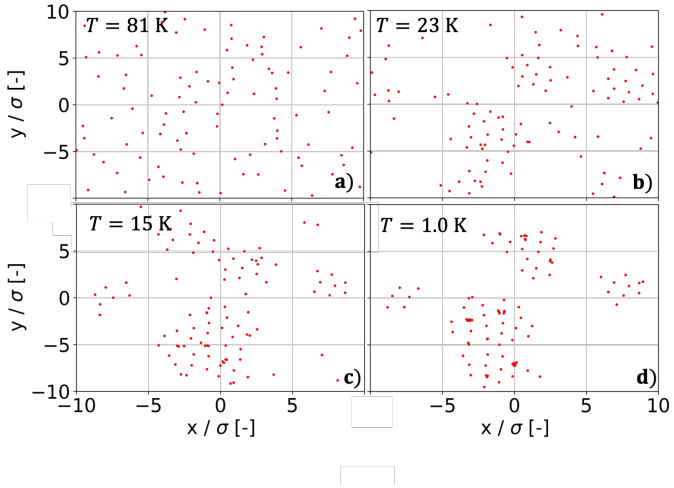

FIG. 4. The four panels display the physical state of the system at different temperatures throughout the cooling process. Hydrogen particles are displayed in red. The horizontal and vertical axis displays the x and y coordinates of the system in units of particle size σ. I.e. if particles are ideally distant, the potential energy is minimised and we expect one particle per unit of e.g. x/σ.

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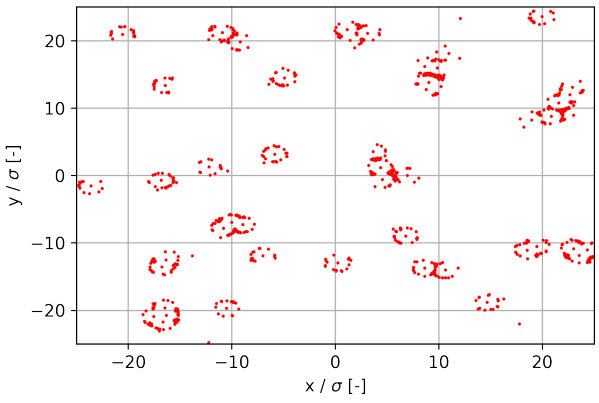

FIG. 5. The physical state of a high density system consisting of $N = 1000$ hydrogen atoms after cooling the system from 100 K towards 0 K.