Generation of nanoporous model using sequential annealing and largest cluster selection method

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Abstract. Using molecular dynamics method, we develop a robust algorithm to generate nanoporous material with considerably natural porous structure. The method consists of sequential heating, relaxation, and quenching of Lennard-Jones meta-material. We vary the binding strength, the equilibrium distance, and the cut-off radius of the interaction potential of each sequence, in order to obtain reasonable melt structure, and agglomeration of the particles into nanowires of the nanofoam. The resulted foamy material has good void and wire size distribution, hence can be applied as target material model on computational study of the physical behaviour of porous materials. The method enables fast creation of the porous media with tuneable values of porosity.

1. Introduction
The importance of porous material spreads from technological application to the phenomena and processes which occurs in nature. Using porous materials one can create light weight substances with tuned physical properties strength, weight, as well as the optical phenomenon such as surface plasmon excitation [1, 2]. In chemical application, the porous material is also used very frequently, for instance in catalytic activities, chemical filters and ion traps [3]. These importance originated from the nature that the medium has large surface area. Usually all the application mentioned above is made possible by laboratory-made porous medium. The procedures involve ion bombardment and laser ablation of materials [4].

In nature, such medium is created by mainly thermal process which consists of heating and cooling of material. Porous rocks is formed by sudden cooling of lava that may be formed when the earth has opening region such as volcanoes and ridges. The porosity of rock is one of decisive parameters, for instance in the surveillance of oil or water reservoir. In this geological and geophysical fields, methods are available to identify porosity, however, the detailed characteristics and structures are still not clearly known.

The theoretical understanding of physical and chemical properties of porous medium is still immature. Studies concerning the properties of such medium is one of the hot topics, especially in the nano-meter scale [5, 6]. In this work we propose a method to produce nano-material model, which can be used for further studies of the properties of porous medium.

2. Method
We used molecular dynamics method to create porous material. The Lennard-Jones meta-material of size 64x64x64 lattice constant was used as the initial crystal with FCC structure. The crystal has the density of 0.89 (in reduced unit) which is the equilibrium density, where the material is in the
minimum pressure. We applied periodic boundary condition to all the side of the crystal. Initially the system consist of 1048576 atoms, and then half number of the atoms is removed in order to induce porosity, remaining 523935 atoms in the system. The position of the removed atom was chosen randomly. In this work we consider a porosity of 50%.

We let the atoms interacting with a high binding energy \( \varepsilon = 20 \) and \( \sigma = 1 \), also used in [5], with cut radius at 2.5 \( \sigma \). This is to make the particles sticking to each other, and prevent too many gas phase formation. The trajectories of particles was followed up to 5000 steps. In this study, we assume, the actual time of the simulation system is not relevant with the real physical condition. After some defined time step we took the crystal to be processed as follows. Firstly, we used the cluster detector algorithm to select the largest connected group of atoms. The smaller clusters are removed from the target system, in order to get one percolated foamy structure. Secondly, the crystallite is relaxed, and let the surface of the filaments in the structure smoothen by the work of surface tension. The relaxation is done through the quenching process to a very low temperature using NPT ensemble. This procedure is applied to snapshots of simulations taken sequentially every 1000 time step. We performed the sequential annealing to various annealing temperature \( T^* \) from 0.1 to 1.0, around the melting temperature of the meta-material, to observe the effect of temperature to the produced porous structure. The method to find the number of clusters inside the simulation system is created following the prescription from [7]. This method has been used in previous works, such as [8, 9, 10]. Let \( i \) and \( j \) define the indices of particles inside a system having randomly distributed clusters. \( C \) and \( A \) represent the enumerated clusters, where the members of a cluster is determined as the connecting particles with maximum inter-particle distance of \( r_{\text{cut}} \). Hence, the cluster criteria is defined as,

(i) If \( i \in C \) and \( r_{i,j} < r_{\text{cut}}^{cl} \) then \( j \in C \)

(ii) If \( A \) is any satisfying criteria (1), and if \( i \) is in both \( A \) and \( C \), then the intersection \( A \cap C = C \)

The cluster detector was written using the binary tree algorithm as can be seen in figure 1. In this algorithm we take a random particle in the system, and calculate the distances between the particle with the neighbouring particles. When the distance is less than or equal the predefined radius, \( r_{\text{cut}}^{cl} \), the pointer of atoms is moved to the neighbour particle. If the visit sequence ends at the first particle and no other neighbouring particles which has \( r < r_{\text{cut}}^{cl} \), all the members of one cluster is counted. The list of particles is then removed from the searching list, and the procedure is restarted from a new randomly picked particle. To make the calculation of distances faster, we utilizes the neighbour-list, which is standard algorithm in molecular dynamics simulation [11].

The resulted porous model can be used as a platform to create crystalline porous target of any material, by mapping the position to the new bulk of crystal. We used LAMMPS code, a scalable molecular dynamics program to run the simulation [12] and Ovito software [13] to do the processing, such as the filling factor and the surface area of the porous media.
Figure 2. Animation of snapshots of the generated porous medium model. Upper row: varied annealing temperature (T*) at #step=1000, lower row: varied annealing time (#step), at T* = 0.1.

3. Result

Figure 2 shows the snapshots of the resulted porous medium model, with varied annealing temperature and sequential time step. On the upper row, we observe the effect of the annealing temperature to the model. Here we find that the porous structure of the model looks similar. Contrary, on the lower row, we see different structure with the same value of porosity. The animation of these snapshots was taken from the annealing simulation with T* = 0.1. The snapshots show that the porous structure depends only weakly to the annealing temperature, but having strong dependence on the annealing time.

Figure 3 shows the surface area and the filling factor of the model. The surface area is defined as the area of the solid surface in the porous model (the yellow surface), and the filling factor is the ratio between the agglomerates (wires) enveloped by the yellow surface, and the void. It is shown in figure 3(a) that the decrease of the surface area follows the Arrhenius law, which decays with the step. The overlap of the plots indicates that the annealing temperature does not affect very much the surface area. Nevertheless, we observe a small rainbow at the higher temperature, which might be due to the thermal behaviour of the meta-material. Figure 3(b) shows the similar trend of the increase of filling factor with the step. This facts demonstrates the small effect of the annealing temperature in the process. The deviation of the filling factor seems to be caused by the thermal expansion.

We now evaluate the effect of the annealing temperature to the filling factor at the longer simulation time. We observe the value at #step=5000, as shown in figure 4. We find a systematic increase of the filling factor, even though, the difference is small. Between T* = 0.1 and T* = 1.25 we have 0.008 filing factor difference, which is insignificant. We assume that this difference is merely due to the larger volume of material at a higher temperature.
Figure 3. The surface area of the porous medium model as a function of (a) annealing time, (b) the filling factor, plotted in several annealing temperature $T^*$ as stated in the legend. The surface area is measured in reduced unit $\sigma^2$.

Figure 4. The filling factor plotted as a function of annealing temperature, at the same time, $\#\text{step}=5000$. The annealing temperature is measured in reduced unit.

In order to get more insight into the dependence of porous model to the annealing temperature and time, we measured the distribution of the solid length. This measurement gives a rough view to the size of wires in the porous structure. We simply create three dimensional grids overlaying the porous model, and count the number of cells which is occupied by particles. The counting stops whenever an empty cell is encountered, and started when a filled cell is found. Assuming the isotropic structure of the model, we only calculate in one axial direction ($z$-direction). The counting result is shown in figure 5.

The peaks in figure 5 indicate the most probable wire size in the model. For $\#\text{step}=2000$ we found the sizes distribute at around length $l = 10 \, \sigma$, which indicate the population of small voids and wires. This can be confirmed by the snapshot on the lower row of figure 2. The distributions of different annealing temperature $T^*$ seems overlapping. Figure 5(b) shows the situation at $\#\text{step}=5000$, where the porous model has coarsened. Even though the lengths experience fluctuation, the peaks are clearly visible. We can see that the wires are dominated by lengths about $l = 12 \, \sigma$, $l = 30 \, \sigma$, and $l = 40 \, \sigma$. This finding shows the coarsening process of the porous model, from the small and homogeneous voids, to the larger in-homogeneous porosity, with wire diameter around $30 \, \sigma$ and $40 \, \sigma$. This indicates clearly that the thermal process induces coarsening of the porous medium models.
4. Conclusion
We found that the porous structure of the model created by annealing process depends strongly on the annealing time, instead of the annealing temperature. The annealing process induces coarsening of porous media, which leads to larger void and filament (wire) size. This shed light on the coarsening mechanism of the porous media, induced by annealing process, which can be potentially applicable on the fabrication porous material with wide range of void size distribution.

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