Supporting Information for

Thermal Bubble Nucleation in Graphene Nanochannels

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S1. Thermal bubble nucleation in Si channels

Figure S1. The extracted nucleation temperature of a heterogeneous system as a function of the channel height.

Figure S1 presents the thermal bubble nucleation temperature dependent on channel height in the confined silicon nanochannel. The increasing trend of nucleation temperature with the decreased channel height in silicon nanochannel is similar as that in graphene nanochannel, while the amplitude of the temperature rise is not so large as that in the graphene nanochannel.

Figure S2. The number density of water molecules with different channel heights at 300 K and under the pressure of 1 bar: channel height of (a) 4.9 nm, (b) 3.1 nm, (c) 2.2 nm, (d) 1.9 nm, (e) 1.3 nm and (f) 0.7 nm.
Figure S2 presents the number density distribution of water molecules along the channel height (z-axis) for nanochannels with height 4.9, 3.1, 2.2, 1.9, 1.3 and 0.7 nm, respectively. The temperature is 300 K and the pressure keeps at 1 bar. Compared with the water number density in graphene nanochannel in Fig. 4, the value of density peak near the solid wall is weak in silicon nanochannel. This indicates that the influence enforced by silicon plate is weaker than graphene plate and then the layering effect of water near the surface of silicon is weaker than that near the graphene plate. The scaling factor $\beta$ in our manuscript can quantitatively describe the interactions between the water molecules with solid material. So, adjusting the scaling factor may stand for the water interacting with different solid materials.

S2. The effects of boundary conditions on thermal nucleation temperature

To test whether the nucleation temperature will be different without fixing the carbon atoms near the water molecules, a nanochannel is constructed as shown in Fig. S3. In this model, the top plate is composed of two layers of graphene and the bottom plate is composed of four layers of graphene. Instead of constraining the second layer graphene in our manuscript, the fourth layer graphene in the bottom plate are fixed without thermal vibration. The rest graphene layers are all kept thermal vibration. As shown in Fig. S4, the simulation results show that the nucleation temperature is approximately the same no matter whether the second graphene atoms vibrate or not in our studied temperature range. This phenomenon is due to that the van der Waals interactions of the second and third graphene layer on the water molecules are really small compared with the first layer, though they are within the cut-off radius.
Figure S3. Schematic of the heterogeneous simulation system. The blue and orange atomic layers represent graphene plates and between the two graphene plates are the water molecules. Periodical boundary conditions are applied along the $x$ and $y$ directions in the heterogeneous simulation system.

Figure S4. The extracted thermal bubble nucleation temperature in heterogeneous systems as a function of the channel height. The red line and the black line represents the nucleation temperature of the heterogeneous system in our manuscript and in Fig. S3, respectively.

S3. Temperature control in a heterogeneous system

A nanochannel is constructed by two pieces of graphene plates as shown in Fig. 1 in the paper. The inner layer of carbon atoms (orange atoms) in the bottom plate is set as the heat source. Heat is injected into the whole system by increasing the temperature of the heat source.
source. The temperature is modulated by using the Langevin thermostat with a time step of 0.1 ps, a leap-frog algorithm is used to integrate the equations of motion.

The Langevin thermostat, the most commonly used thermostat in NAMD, controls temperature well. In detail, Langevin dynamics is a means of controlling the kinetic energy of the system, and thus, controlling the system temperature. The method uses the Langevin equation for a single particle:

\[
\frac{m_i}{t^2} \frac{d^2 x_i(t)}{dt^2} = F_i(x_i(t)) - \gamma_i \frac{dx_i(t)}{dt} m_i + R_i(t)
\]

Here, two additional terms on the right hand side accompany the ordinary force the particle experiences. The second term represents a frictional damping that is applied to the particle with frictional coefficient. The third term represents random force which act on the particle (as a result of solvent interaction). These two terms are used to maintain particle kinetic energy to keep system temperature, for instance, at a constant value.

**S4. Thermal bubble nucleation in a homogeneous system**

![Figure S5](image_url)

**Figure S5.** Schematic of the homogeneous simulation system. The homogeneous system has the same number of water molecules with the heterogeneous system at 300K under the external pressure of 1 bar. Periodical boundary conditions are applied along the x y and z directions in the homogeneous simulation system.
In this paper, we use MD simulations to show the thermal bubble nucleation process in a homogeneous system with the NPT ensemble. At the beginning, the water molecules are initialized in the liquid state as shown in Fig. S5. During the simulation process, the system is firstly energy minimized for 1 ns, followed by 2 ns NPT equilibration at 300K under the external pressure of 1 bar. Then the temperature of the system is increased to a preset value, and the simulation is evolved for another 10 ns. The volume change in the system is observed. When the temperature is below the nucleation temperature, the volume of the system increases slightly with the rise of temperature due to thermal expansion. With the system temperature rising to the phase transition temperature of water, the system volume increases dramatically. If thermal bubble nucleates, the presetting value of the system temperature gradually reduces until no phase transition occurs in the simulation time lasting 10 ns and the system temperature drops to a certain value. The minimum temperature at which nucleation occurs is defined as the nucleation temperature.

S5. The potential energy in the heterogeneous and homogeneous system

The NPT ensemble is used in our simulation, in which the temperature is a control parameter. Even the same temperature is set for the heterogeneous system and the homogeneous system, the real temperatures in the two systems are not identical. Different temperatures in the two systems induce the potential energy difference. More details are given below.

In our manuscript, the potential energy for the homogeneous and heterogeneous systems is calculated from two molecular dynamics simulation systems as described in Fig. 1. The heterogeneous system is constructed by sandwiching water molecules with two graphene plates, while the homogeneous simulation system is constructed by removing the two graphene plates from the heterogeneous simulation system. The homogeneous system has the same number of water molecules with the same temperature.

NPT ensemble is used for both heterogeneous and homogeneous cases. Given the number of the atoms and external pressure, the control parameter is the temperature $T$ for a NPT system. Although the temperature is given the same for both the heterogeneous and homogeneous systems, temperature fluctuations are inevitable for both systems. Figure S6 presents the temperature distribution along $z$-direction in heterogeneous and homogeneous systems, respectively. In the heterogeneous system, the temperature near the wall fluctuates greatly and the average value of the water remains around 300K. While in the homogeneous
system, the temperature fluctuation is small. Figure S7 is an enlarged diagram of Fig. S6. As shown in Fig. S7a, c, the average temperature of the heterogeneous system in the region near the wall is lower than that of the homogeneous system because of the wall effect. In order to maintain the average temperature of the system at 300K, the average temperature of the central region in the heterogeneous system is higher than that of the homogeneous system, as shown in Fig. S7b. In Fig. S8, we calculate the potential energy distribution along z-direction in heterogeneous and homogeneous systems. Figure. S8b presents the center region in Fig. S8a. In theory, the potential energy of the homogeneous system should be the same as that in the central region of the heterogeneous system, given the same temperature for the two systems. However as shown in Fig. S8b, the average potential energy in the homogeneous system is a little bit lower than that at the center region of the heterogeneous system, where the red line stands for the average potential energy of center part in heterogeneous case and the black line for the potential energy in homogeneous system. The gap between two lines is distinct, which will lead the potential energy in the heterogeneous system is a little bit higher than that in the corresponding homogeneous system. Increasing the system size does not change the temperature profiles across the whole channel in the heterogeneous system for a MD model. So, the specific potential energy in the heterogeneous system is a little bit higher than the homogeneous system, which is attributed to the minor temperature difference in the two systems. This difference is due to the limited system size studied in our simulation systems. If the system size enlarges, this difference should reduce and even disappear when the system size is large enough.

**Figure S6.** The temperature distribution of water molecules along the z direction at 300 K and under the pressure of 1 bar with channel height 4.9 nm in heterogeneous case and homogeneous case.
Figure S7. The temperature distribution of water molecules along $z$ direction at 300 K and under the pressure of 1 bar with channel height 4.9 nm in heterogeneous case and homogeneous case. The red dot line presents the average temperature of the heterogeneous system and the black dot line presents the average temperature of the homogeneous system.

Figure S8. (a) The red line represents the potential energy distribution of water molecules along $z$ direction with channel height 4.9 nm of the heterogeneous system at 300 K and under the pressure of 1 bar. The black line is the potential energy distribution of the homogeneous system. (b) The red dot line is the average potential energy of center part in the heterogeneous system and the black dot line is the average potential energy of the homogeneous system.

S6. The effects of the channel height on the nucleation temperature when the channel height below 3.1 nm
Figure S9. The number density and the potential energy distribution of water molecules along z direction at 300 K and under the pressure of 1 bar: channel height of (a) 4.0 nm, (b) 3.1 nm, (c) 2.6 nm, and (d) 2.2 nm.

An interesting finding is that the sharp increase in the nucleation temperature when the channel height below 3.1 nm. This is true as observed in Fig. 3 in our manuscript. The reason is attributed to the van der Waals interaction range. As demonstrated in Fig. 6, once the channel height is below 3.1 nm, the potential energy in the heterogeneous system is obviously smaller than that corresponding to the homogeneous system. Carefully comparing Fig. 3, Fig. 4 and Fig. 6, we can find the thermal nucleation temperature strongly depends on the potential energy. As shown in Fig. 4a, the near-wall layering structure of water molecules is about 1.1 nm thick away from the mass center of the inner graphene sheet. When the channel height is below 2.2 nm, all of the water molecules behave as solid-like structure, corresponding to that the specific potential energy decreases and the thermal bubble nucleation temperature increases synchronously. When the channel height is between 2.2 nm and 3.1 nm, the potential energy of water molecules in the heterogeneous channel is slightly lower than that in the homogeneous system. Thus, the nucleation temperature in the heterogeneous system is slightly higher than that in the homogeneous system. Once the channel height is higher than 3.1 nm, the ratio of the water molecules in the near wall region to the total water molecules in
the heterogeneous system becomes small. Continually increasing the channel height, the central part of the water molecules behave the properties as a quasi-homogeneous system including water density and potential energy.

As shown in Fig. S9a, b, when the channel height is above 3.1 nm, several layers of ordered water molecular structure near the solid wall can be formed due to the wall effects, leading to the near-wall layering structure. While the water molecules in the central region of the channel are unaffected and present the similar bulk characteristics. When the channel height is below 3.1 nm, the layering structure penetrates gradually through the entire liquid system, which means that all water molecules will form more ordered arrangement as shown in Fig. S9c, d. In Fig. 6 in our paper, the heterogeneous systems specific potential energy decrease drastically for the channel height below 3.1 nm. In addition, the confined effect is stronger with the smaller channel height, which leads to a lower system potential energy. This is why the nucleation temperature increases sharply for the channel height below 3.1 nm.

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