

INVESTIGATION OF THE FLUID IN A VACNF ON THE NANOLEVEL SCALE USING A MOLECULAR DYNAMICS SIMULATION

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Introduction

Vertically arrayed CNT forests (VACNFs) have attracted great attention; because they can be made on a large scale at low cost by chemical vapor deposition, and their mesoporous structures have a high potential for use in nanofluidic applications, such as nanofiltration, biosensor and catalyst. In the design of these nanofluidic equipment based on CNTs, it is essential to understand and control the interaction between the CNTs and the fluid. For that reason, many investigations of water permeation inside a CNT have been carried out analytically and experimentally. It has reported that the flow rates of water through a CNT are one to five orders of magnitude greater than those predicted by the continuum-based no-slip Hagen-Poiseuille relation. Furthermore, these flow rates increase as the area of the permeation region decreases. Although the flow investigations inside a CNT are done analytically and experimentally, no experimental investigations have been done on the outside of a CNT in a VACNF. Thus, in the present study, we simulated the permeation of water fluid, which is at an unsaturated state, outside a CNT in a VACNF, and investigated the flow of water. Here, we used the Gebart model as permeability model of porous medium, which is known for its consistency with experiments and continuum numerical analyses. However, the fluid inside minute porous on a nanolevel involves a high Knudsen number (Kn), and the flow turns into a slip flow, which has a velocity in the liquid/solid interface. Thus, there is a possibility that the Gebart equation cannot be applied to a fluid in a nanopore; however this has not been confirmed yet. Our research goal is to verify the application of the Gebart equation by comparing the permeabilities of the Gebart equation (no-slip model), derived using a hypothesizing Hagen-Poiseuille flow, and the Darcy's law using MD results (actual model), and the verification of flow tendency in a nanopore.

Fuild permeation outside CNTs and Analytical model

In the evaluation formula of fluid permeation, we use the permeability in the Darcy's law (eq. (1)) and the Gebart equation (eq. (2)) which are widely used to verify the permeation behavior of a fluid in a porous media. Here, when we calculate the permeability using MD results, we use Darcy's law.

$$u_{MD} = - \frac{K_{MD}}{(1 - V_C)\mu_{MD}} \frac{dP}{dz} \quad (1)$$

$$K_G = - \frac{8R^2 (1 - V_C)^3}{57 V_C^2} \quad (2)$$

Where u_{MD} is the velocity of fluid permeation into porous media, K_{MD} is the permeability, dP/dz is the pressure gradient in the flow direction, K_G is the permeability of the case that the permeation direction is parallel to the fibrous direction, R is the fiber radius and V_C is the volume fraction of a CNT. Here, we predict the viscosity from the axial self-diffusion coefficient, D , by evoking the Einstein relation [1].

$$\mu_{MD} = \frac{k_B T}{6\pi a D} \quad (3)$$

$$\lim_{t \rightarrow \infty} \langle |\mathbf{r}(t' + t) - \mathbf{r}(t')|^2 \rangle = 6Dt \quad (4)$$

Where k_B is the Boltzmann constant and a is the molecular diameter, T is the temperature and \mathbf{r} is the position of molecule. The analytical model of permeation outside the CNT is shown in Fig. 1(a), and we

set the CNT with a cap in the center of graphene, and arranged water molecules above the CNT. The CNT diameter is 2.16 nm, and its length is 3.19 nm. We varied the size of the graphene to reach $V_C = 0.077, 0.090, 0.106, 0.188, 0.311, 0.424, 0.505, 0.611, 0.706$ and 0.780 . Here, we defined V_C as $V_C = (\text{area of CNT}) / (\text{area of graphene})$ in the model of Fig. 1(a). By applying the boundary conditions to the analytical model in Fig. 1(a), we created the VACNF shown in Fig. 1(b).

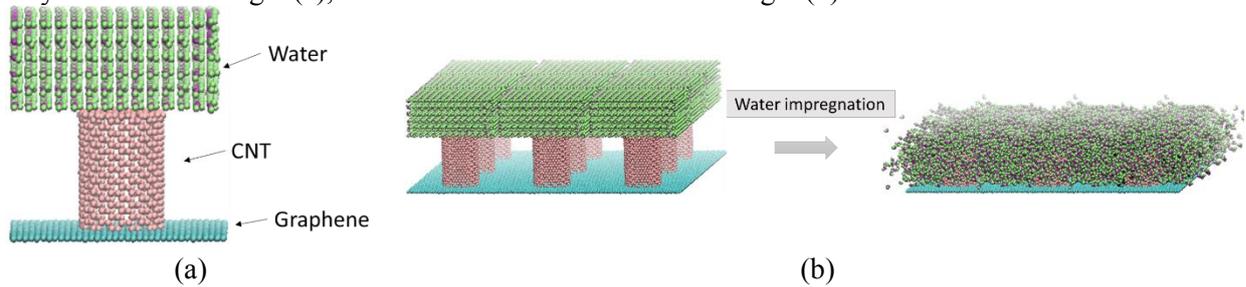


Fig. 1 Analytical models and permeating behavior. (a) Analytical model of impregnation outside a CNT. (b) Impregnation is performed by applying the periodic boundary condition.

Results and Discussion

We show the results of the MD simulation and the calculation in Fig. 2. We make three analysis attempts for each V_C , and the data in each of the figures are its average values. First, In Fig. 2(a), Kn is higher than 0.001 for each V_C , thus it is found that the water flow becomes slip flow. Furthermore, Kn and viscosity increase as the permeation area becomes narrower. Then, Fig. 2(c) shows the relationship between V_C and permeability ($\log K$). In this graph, although the permeability of the actual state using MD results increase, that of no-slip state decreases as the permeating area becomes narrower. On the other hand, the permeability of the actual state using the MD results corresponds with that of the no-slip state as the permeation area becomes wider, that is, the influence of slip becomes smaller. Thus, we can state that a clear divergence in the permeability tendency occurs between the slip and no-slip states, and a wide region exists in V_C where permeability in the no-slip state cannot be applied in nanopore-based CNTs. Furthermore, we find that water more easily permeates as V_C increases in the actual state. This is because almost no friction is generated by the super-hydrophobicity of the CNT, and weak interfacial forces exist between the CNT and the water molecules.

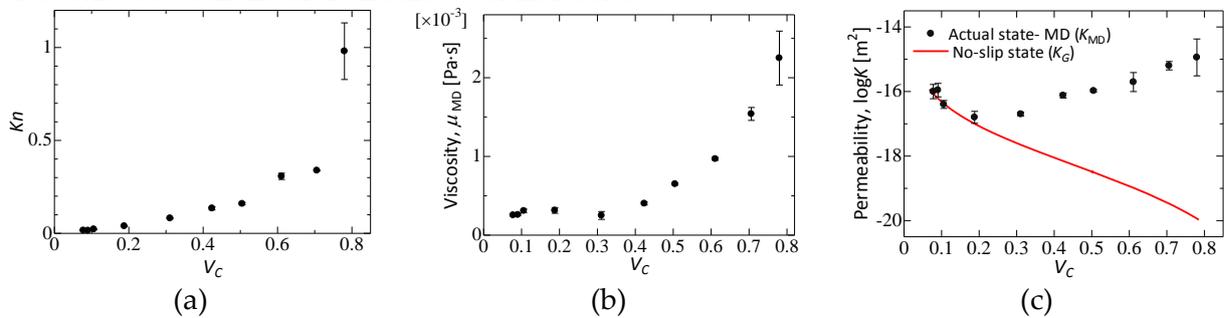


Fig. 2 Results of MD simulation. V_C vs (a) Kn , (b) viscosity and (b) permeability.

Conclusions

In this study, we conducted a MD simulation of introduction of water into VACNFs. As a result, we acquired the following results. First, Kn increased as the permeation area become narrower. Moreover, for each V_C , Kn was greater than 0.001 where the flow becomes slip flow. Next, while the permeability of the slip state from the MD results increases, that of the no-slip state decrease as the permeating area becomes narrower. On the other hand, the permeability of the slip state using the MD results corresponds with that of the no-slip state as the permeation area becomes wider, that is, the influence of slip becomes smaller. Thus, we can conclude that there is a clear divergence of permeability tendency between the slip state and the no-slip state. Furthermore, it is found that the V_C increases and water permeates more easily owing to the influence of the super-hydrophobicity of the CNT and the weak interfacial forces between the CNT and the water molecules.

References

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