Effect of soft repulsive wall on the bulk phases of thermotropic liquid crystals

Jagroop Kaur, and Debabrata Deb

ARTICLES YOU MAY BE INTERESTED IN

Hydration characteristics of fullerene in water: A coarse-grained molecular dynamics simulation study
AIP Conference Proceedings 2265, 030043 (2020); https://doi.org/10.1063/5.0017486

Pressure induced phase transition and super conductivity of Th$_2$C$_3$: An ab-initio study
AIP Conference Proceedings 2265, 030017 (2020); https://doi.org/10.1063/5.0017545

Effect of temperature on the molecular vibrations of linear and branched polyethylene
AIP Conference Proceedings 2265, 030038 (2020); https://doi.org/10.1063/5.0017321
Effect of Soft Repulsive Wall on the Bulk Phases of Thermotropic Liquid Crystals

Jagroop Kaur and Debabrata Deb

1(Thapar Institute of Engineering & Technology, Bhadson Road, Patiala, Punjab-147004, India)

a)Corresponding author: (debabrata.deb@thapar.edu)

Abstract. Using the computer simulations, the effect of soft repulsive wall on a system comprising of thermotropic liquid crystalline material is studied. We place the walls perpendicular to the z-axis at the ends of an anisotropic box with the periodic boundary conditions along x and y axes. Here, the wall interaction strength, temperature and density are the control parameters. We analysed the effect of temperature on the system confined by the wall at different number densities. Within a limited range of temperatures, we observe that temperature is actually a good control parameter in the system. Moreover, the effect of wall on the system is more pronounced at low number densities.

INTRODUCTION

Nucleation phenomenon is widespread in nature, for example, the formation of clouds, snowflakes, bubbles, foams in drinks, etc. The understanding of nucleation of different phases of a material (e.g. from a fluid to crystal) is very important because of its applications in material processing. We have achieved a good understanding of the homogeneous nucleation. In contrast, there are still plenty of open questions when it comes to heterogeneous nucleation process, where the nucleation is facilitated by a third agent apart from the two phases. This third agent could be any kind of impurity, a probe or simply a wall which is holding the materials. In this article, we demonstrate some effects of a soft repulsive wall on the attached material. Generally speaking, the presence of a fluid near a wall leads to various interfacial phenomena like wetting, adhesion, and heterogeneous nucleation. The wetting and drying of fluids over the solid surfaces plays a crucial role in several natural phenomena such as formation of ice crystals in the atmosphere, solidification of molten silicates in processes deep inside the earth’s crust, industrial processes like formation of thin polymeric films, paints tailored to stick better on the surfaces and development of drugs to improve their effectiveness. To understand all these processes is to understand how a liquid behaves over surfaces, why and when a liquid wets a surface. During the condensation of a saturated gas over the solid substrate, a small amount of liquid formed over the surface coexists with the gas. In this process, liquid either may exist in the form of droplets touching the surface with a well-defined contact angle $\theta$ or it may spread out into a homogeneous film on the surface. A ‘complete wetting’ occurs when the contact angle is $\theta = 0$ (Young’s angle) and the liquid immediately undergo condensation, starts growing over the surface and then completely coats it, and thus remaining vapor does not remain supersaturated. However, in the case of ‘complete drying’ of the wall or $\theta = \pi$, the fluid particles do not get attracted to the surface, rather it prefers the vapor phase. However, the most interesting case occurs for the intermediate situation of ‘incomplete wetting’ ($0 < \theta \leq \pi/2$) or ‘incomplete drying’ ($\pi/2 \leq \theta < \pi$). The heterogeneous nucleation of spherical particles, colloid-polymer mixtures, lattice gas model using hard/soft/structured walls have been extensively studied using computer simulations. But in reality, the molecular materials are mostly made up of anything but spherical particles. Therefore, there is a need to understand the interfacial phenomenon in the case of aspherical particles. In this paper, we have used the Gay-Berne (GB) interaction potential to model ellipsoidal particles that are placed near a soft repulsive wall and the computer simulations are done using molecular dynamics simulation techniques. We have varied both the applied temperature
and system density and broadly observed that such a wall facilitates the formation of smectic (crystalline) layers parallel (or normal) to the wall.

MODEL AND SIMULATION DETAILS

The Gay-Berne (GB) pair potential is used to model the liquid crystalline particles. Each molecule $i$ is considered as a rigid unit which is axially symmetrical and is represented by the position of its center of mass $r_i$ oriented along the direction of the primary axis with an unit vector $e_i$. The GB pair potential between the molecules $(i,j)$ is given by

$$U^\text{GB}(r_{ij}, e_i, e_j) = 4\varepsilon_{ij}(r_{ij}^{-12} - r_{ij}^{-6})$$

with $q_{ij} = \frac{r_{ij}^2 - \sigma(\beta r_{ij} e_i e_j) + \sigma_0}{\sigma_0}$. Here, the constant $\sigma_0$ defines the molecular diameter, $r_{ij}$ is the distance between the centers of mass of molecules $i$ and $j$, and $e_i = r_{ij}/r_{ij}$ is a unit vector along the vector $r_{ij} = r_i - r_j$. $\sigma(r_{ij}, e_i, e_j)$ is the distance (for given molecular orientations) at which the intermolecular potential vanishes, and is given by

$$\sigma(r_{ij}, e_i, e_j) = \sigma_0 \left\{ 1 - \frac{X}{2} \left[ \frac{(r_{ij}^2 + r_{ij}^2)^2}{1 + \chi(r_{ij}^2 e_i e_j)^2} + \frac{(r_{ij}^2 - r_{ij}^2 e_i e_j)^2}{1 - \chi(r_{ij}^2 e_i e_j)^2} \right] \right\}^{-1/2}$$

Here, $\chi = (k^2 - 1)/(k^2 + 1)$ and $\sigma = \sigma_a/\sigma_0$, is the measure of length to breadth ratio of ellipsoidal molecule (known as aspect ratio). The molecular diameters along the secondary axis and primary axis (main symmetry axis) are $\sigma_a = \sigma_0$ and $\sigma_a$, respectively. Also $\varepsilon(r_{ij}, e_i, e_j) = e_0 [\varepsilon_1(e_i, e_j)]^{1/2} [\varepsilon_2(r_{ij}, e_i, e_j)]^{1/2}$, with $\varepsilon_1(e_i, e_j) = \left[ 1 - \chi^2(e_i \cdot e_j)^2 \right]^{-1/2}$,

$$\varepsilon_2(r_{ij}, e_i, e_j) = 1 - \frac{k}{2} \left[ \frac{(r_{ij}^2 + r_{ij}^2 e_i e_j)^2}{1 + \chi(r_{ij}^2 e_i e_j)^2} + \frac{(r_{ij}^2 - r_{ij}^2 e_i e_j)^2}{1 - \chi(r_{ij}^2 e_i e_j)^2} \right]$$

where the overall energy scale of the pair interactions is set by the parameter $e_0$, $\chi' = (k^{1/2} - 1)/(k^{1/2} + 1)$ and $\chi'' = \sigma_a^2/\varepsilon_{ee}$ where the potential depth for side-to-side aligned molecules is $e_a$, and that of the end-to-end aligned molecules is $e_{ee}$. Here, $\mu$ and $\nu$ are the adjustable exponents. We take the set of the four parameters ($k$, $k'$, $\mu$, $\nu$) as $(3, 5, 2, 1)^{1,12}$ which are the most used parameters in various studies for GB potential. The value of cut off radius, $e_0$ and $\sigma_0$ are taken to be 4.1 and 1 respectively. All parameters are taken in reduced units. The particles with unit masses and diameters 1, 1 and 3 along x, y and z axes are taken.

To perform the computer simulations, we take an anisotropic cuboidal box with its elongation along the z-axis. The length of the box along the x-axis ($L_x$) is equal to its length along the y-axis ($L_y$) and is almost half of the length along the z-axis ($L_z$) i.e. $L_x = L_y = L_z/2$. Initially, the system of $N = 16000$ number of GB particles with a very low density of 0.01 is taken. The initial velocities and orientations are randomly assigned to the particles (according to the Gaussian distribution). The whole simulation scheme to obtain an equilibrium system includes three steps. Firstly, the NPT simulations are performed at high-pressure to get a system with a high number density ($10^7$ steps). Secondly, the NVT simulations are performed for $10^7$ steps more. Following this, two soft and repulsive walls (Weeks-Chandler-Anderson (WCA) potential) are placed at the ends of the box perpendicular to the z-axis. Then, again the NVT simulations are performed with walls for $10^7$ steps. The first and second steps are performed with timestep size 0.005 and the third step is run with timestep size 0.002. The whole recipe is performed for two temperatures, $T=0.8, 1.0$. The simulations at different number densities are then performed by deleting the particles from the system resulted after the second step for both temperatures.

RESULTS AND DISCUSSION

For the set of densities and temperature that we have studied and presented below, bulk properties the system confined by two walls at two ends remains overall in the same as in the case of the system without the walls. For example, in Fig 1(a), at $T=0.8$ and $\rho=0.345$, the bulk (center of the box) phase is the isotropic liquid and the same phase is also observed when the system with same density and temperature is simulated in the absence of wall (data not shown). But the order of the particles away from bulk and close the walls are changed and observed to form layers parallel to the walls as shown in the series of snapshots Fig. 1(a)-(f). The soft smooth walls act as a template and the GB particles wet the wall with an increasing number of layers as the density is increased. It is also evident that the lower the temperature the more the number of layers are formed (compare any two snapshots in Fig. 1 corresponding to the same row except the Figs. 1. (g) and (h)). This is understandable, as the temperature is lowered (left column of Fig. 1), the system is facilitated to acquire more order and the system does this by forming more of
highly ordered smectic layers next to the wall. At the lower temperature (T=0.8) and in denser systems, there are competing domains of smectic phase-oriented in different directions. It is also very intriguing to observe that at very high density and low temperature (Fig. 1 (g), the wetting behavior of the materials has changed and now only a single layer is formed parallel to the wall showing a reduced effect of the wall. It would require further simulations and analysis to understand why and how such domains are formed in confined systems and which parameter is more useful than the other to manipulate the wetting behavior. As for thermotropic LC, both the temperature and density are control parameters and we have seen some of their effects in Fig 1 (a)-(h). Moreover, in case of a wall confined system, the wall strength is also another possible parameter, hence it would also be very useful to see how the nature and strenght of the wall-particle interaction affect the wetting behavior. As mentioned above, to proceed further, to understand the wall induced heterogeneous nucleation phenomena, the next step is to calculate the wall-material interfacial energy, which is going to be our next step forward.

(a) T=0.8, ρ = 0.3137
L_x = L_y = 27.98, L_z = 58.21,

(b) T=1.0, ρ = 0.3137
L_x = L_y = 27.98, L_z = 58.21

(c) T=0.8, ρ = 0.3237
L_x = L_y = 27.98, L_z = 58.21

(d) T=1.0, ρ = 0.324
L_x = L_y = 27.98, L_z = 58.21,

(e) T=0.8, ρ = 0.3324
L_x = L_y = 27.98, L_z = 58.21,

(f) T=1.0, ρ = 0.3325
L_x = L_y = 28.06, L_z = 58.38,
FIGURE 1. The snapshots of anisotropic box containing Gay-Berne particles with walls at the two ends (left and right) of the box at T=0.8, 1.0 are shown.

CONCLUSION

From the above findings, we infer that the temperature is a good control parameter for the system comprising liquid crystalline particles and confined with soft and repulsive walls. These walls aid the particles to align in a direction along the normal to the wall. At low temperature and low density, the wall affects the system and rearrange the particles. But at high densities, the wall has very little effect on the system and at high temperature, the wall has its effect on the system which it loses at low temperature. Such unusual results at high densities need to be studied further which will be done by calculating the free energy difference between the isotropic and wall-confined anisotropic systems.

REFERENCES

6. T. Young, Phil. Trans. R. Soc. 85 (1805).