Why are Fluid Densities So Low in Carbon Nanotubes?

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The equilibrium density of fluids under nanoconfinement can differ substantially from their bulk density. Using a mean-field approach to describe the energetic landscape near the carbon nanotube (CNT) wall, we obtain analytical results describing the lengthscales associated with the layering observed at the fluid-CNT interface. When combined with molecular simulation results for the fluid density in the layered region, this approach allows us to derive a closed-form prediction for the overall equilibrium fluid density as a function of the CNT radius that is in excellent agreement with molecular dynamics simulations. We also show how aspects of this theory can be extended to describe water confined within CNTs and find good agreement with results from the literature.

Fluids under nanoscale confinement exhibit many remarkable properties [1,2]. In particular, if a carbon nanotube (CNT) is in equilibrium with a fluid bath, the density of the fluid inside the CNT can differ dramatically from the density of the bulk fluid – in the case of nanoconfined water, this density can be as low as 200 kg m$^{-3}$ [4]. Understanding and predicting this anomalous density is very important for a variety of applications, such as designing nanoscale desalination devices [5], engineering nano-syringes for drug delivery across cell membranes [6], calculating shale gas content of nanoporous rock [7], and explaining flow rates in nanochannels [8]. From a computational point of view, predicting equilibrium densities under confinement can be very beneficial for the simulation of nanofluidic systems because it allows realistic simulation of such systems without coupling to an external fluid bath [9,11]. Benefits are also possible when a fluid bath is included: for example, it is common to pre-fill nanopores with fluid molecules to reduce equilibration time; knowledge of the correct density minimizes the computational cost associated with equilibration.

Several MD studies have investigated modified equilibrium densities under nanoconfinement [4,9,12,13], but there is currently no first-principles model that can predict this density without the high computational costs of a density-functional theory calculation [14]. We present here an energetics approach that accurately predicts the density of a Lennard-Jones (LJ) fluid confined in a CNT. We compare the results of this model to MD simulations and find excellent agreement. We also show that certain aspects of this theory can be extended to water confined within CNTs; again, excellent agreement with MD simulations is observed.

It is well known that fluids confined within a sufficiently large CNT will form concentric rings near the CNT wall [4,9,13]. Near the center of the CNT, the fluid will exhibit little ordering and resemble bulk fluid i.e. fluid that is not “aware” of the presence of the CNT wall. These features can be seen clearly in Fig. 1. In what follows, we develop a mean-field theory for describing this structure, which will also allow us to predict the equilibrium fluid density inside a CNT as a function of its radius.

In this work we focus on intermolecular interactions governed by the Lennard-Jones potential [15] with parameters $\varepsilon$ and $\sigma$ used here to denote interactions between a fluid molecule and a wall carbon; $\varepsilon_f$ and $\sigma_f$ will denote interactions between fluid molecules.

Assuming that the CNT is sufficiently long compared to its radius $R$, we can derive a mean-field interaction potential between the CNT wall and the fluid by integrating the LJ potential around the cylindrical geometry of the CNT [16] to obtain:

$$\mathcal{V}(r) = n\pi^2\varepsilon\sigma^2\left[\frac{63}{32} F_{\frac{3}{2};-\frac{3}{2};1}(\delta^2)(\frac{R(1-\delta^2)}{\sigma})^{-10} - 3F_{\frac{3}{2};-\frac{3}{2};1}(\delta^2)(\frac{R(1-\delta^2)}{\sigma})^{-4}\right]$$

(1)

Here, $n$ denotes the areal density of carbon atoms in the CNT wall, $\delta$ the normalized radius $\delta \equiv r/R$, and $F_{\alpha;\beta;\gamma}(z)$ the Gauss hypergeometric function. In what follows, $F_{\eta}(z)$ will denote $F_{\eta;1}(z)$.

The mean-field potential for a variety of CNT radii is shown in Fig. 2. As expected, it rises sharply as $r \rightarrow$
serting the above expression for $\sigma/R$ from the CNT wall. This choice is motivated by the 

\[
\delta = \text{solve, we write} \\
\text{out of the problem and thus} \\
\varepsilon \text{This equation shows that the parameter} \\
\text{molecules is expected to be a reasonable approximation}
\]

$R$, thus leading to a stand-off distance that defines the outer edge of the outer fluid ring; this will be referred to as $r_{\text{max}}$, the “maximum accessible radius.” The outer ring can be fully defined by $r_{\text{max}}$ and $r_{\text{min}}$, where the latter denotes the inner edge of the ring. We will invoke symmetry to show that $r_{\text{min}}$ can be calculated as $2r_{\text{avg}} - r_{\text{max}}$, where $r_{\text{avg}}$, as shown in Fig. 2, is the location of the mean-field potential minimum. Calculation of these quantities, as well as extension of these arguments to the calculation of subsequent rings is given below.

We calculate the maximum accessible radius $r_{\text{max}}(R, \sigma, \varepsilon, T)$ by finding the location at which most of the liquid molecules have insufficient kinetic energy to overcome the potential barrier $\Psi(r)$. The steep rise of $\Psi(r)$ close to $r = R$ (where $r_{\text{max}}$ is expected to lie), allows us to approximate this location by $\Psi(r_{\text{max}}) = 0$ with little error. Neglecting the thermal energy of liquid molecules is expected to be a reasonable approximation for typical LJ parameters $\varepsilon$ and $\sigma$ and temperature $T$. A direct consequence is that our solution for $r_{\text{max}}$ is independent of the temperature; this is in excellent agreement with our simulation results. Setting $\Psi(r_{\text{max}}) = 0$, we can rearrange (1) into

\[
\frac{21}{32} \sigma^6 = R^6 \left(1 - \delta_{\text{max}}^2\right) \frac{6F - \frac{1}{2} \left(\delta_{\text{max}}^2\right)}{F - \frac{1}{2} \left(\delta_{\text{max}}^2\right)}
\]

This equation shows that the parameter $\varepsilon$ can be scaled out of the problem and thus $\delta_{\text{max}} = \delta_{\text{max}}(R, \sigma)$. To solve, we write $\delta_{\text{max}}(R, \sigma) = 1 - k_{\text{max}}(R, \sigma)(\sigma/R)$, where $k_{\text{max}}(R, \sigma)(\sigma/R)$ is the normalized “stand-off” distance from the CNT wall. This choice is motivated by the expectation that this distance will be of order $\sigma/R$. Inserting the above expression for $\delta_{\text{max}}$ in (2) we obtain to leading order \[ k_{\text{max}}(R, \sigma) = (2/5)^{1/6}, \] which yields

\[
r_{\text{max}}(R, \sigma) = R - (2/5)^{1/6} \sigma
\]

This result is in agreement with but also explains previous MD simulation results by other groups \[ 15, 19. \] We note that the leading-order solution obtained here is equivalent to neglecting the effect of CNT curvature, explaining why the stand-off distance is not a function of $R$. Although higher-order solutions are possible, the excellent agreement of (3) with numerical solution of (2) as well as MD simulations for essentially all CNT radii of interest (Fig. 3), suggests that this is unnecessary.

We calculate the average radius of the outer ring, $r_{\text{avg}}$, as the location of the minimum of $\Psi(r)$, given by

\[
\delta_{\text{avg}} \left[ \frac{81F - \frac{1}{2} \left(\delta_{\text{avg}}^2\right)}{2(1 - \delta_{\text{avg}}^2)^{10}} + \frac{20F - \frac{1}{2} \left(\delta_{\text{avg}}^2\right)}{(1 - \delta_{\text{avg}}^2)^{11}} \right] - \\
\frac{32\delta_{\text{avg}}}{21\sigma^6 R^6} \left[ \frac{9F - \frac{1}{2} \left(\delta_{\text{avg}}^2\right)}{2(1 - \delta_{\text{avg}}^2)^4} + \frac{8F - \frac{1}{2} \left(\delta_{\text{avg}}^2\right)}{(1 - \delta_{\text{avg}}^2)^5} \right] = 0
\]

By writing $\delta_{\text{avg}}(R, \sigma) = 1 - k_{\text{avg}}(R, \sigma)(\sigma/R)$, we can approximate (4) by

\[
\frac{21}{32} \sigma^6 = \frac{18}{\pi} + \frac{256}{35\pi} R \left(2k_{\text{avg}}\right)^{-1} - \frac{524288}{63\pi} R \left(2k_{\text{avg}}\right)^{-7}
\]

Neglecting terms smaller than $O(R/\sigma)$ (thus again neglecting the effect of curvature), we find that $k_{\text{avg}} = 1$. By symmetry, the inner radius of the outer ring is given by $R - k_{\text{min}} \sigma$, where

\[
k_{\text{min}}(\sigma) = 2 - (2/5)^{1/6}
\]

We can observe from Fig. 1 that several distinct fluid rings form before relaxation to bulk structure occurs. We model the formation of additional rings within the outermost ring by arguing that the outermost ring itself can be treated as another nanotube. This general approach of recognizing that cylindrical solid structure induces concentric near-solid ordering in adjacent fluid has been pursued with success by Wilson in numerous MD studies \[ 20, 21. \]

In particular, if we denote the outermost ring as $r^{(1)}$, we predict that the second ring will have an outer radius of $r^{(2)} = r^{(1)} - k_{\text{max}}\sigma f$ and an inner radius of $r^{(1)} - k_{\text{min}}\sigma f$. This process can be repeated indefinitely to fix outer and inner radii for the $n$-th ring $r^{(n)}$, but in practice this method loses meaning after the outer radius of the $(j + 1)$-st ring is greater than the inner radius of the $j$-th ring, at which point the rings are “blurred” into a more uniform background bulk structure. For the purposes of this study, we will only consider two rings (in addition to the bulk core), but the technique can, in principle, be generalized to arbitrarily many rings. In Fig. 4 we observe that these analytical
FIG. 3. Comparison between theoretical prediction for maximum accessible radius (3), numerical solution of (2), and maximum accessible radius from MD simulations.

FIG. 4. Theoretical prediction for ring locations in a CNT (R = 17.61 Å) and radial density profile from MD simulation.

expressions provide very good estimates of the locations and characteristic widths of the two outermost rings.

We now show that combining these predictions on the ring structure with information about the fluid density inside the rings can be used to develop a closed-form expression for the equilibrium fluid density inside CNTs. Remarkably, the results presented below are valid for a wide range of reservoir densities; specifically, our MD simulations show good agreement with these results in the range $0.8 \sigma_f^{-3} \leq \rho_{\text{bulk}} \leq 1.1 \sigma_f^{-3}$. To capture this generality, we report fluid densities relative to (normalized by) the bulk density.

The fluid density in ring $i$ is defined as the number of fluid-molecular centers falling within the range $[r_{i,\text{min}}^2, r_{i,\text{max}}^2]$, divided by the volume enclosed by this region. We note that this simple definition captures over 95% of molecules in the ring region; the small number of remaining molecules are assigned to the nearest ring. By averaging results for ring densities over the range of simulated CNT radii, we find that the density for the first two rings remains invariant for a wide range of conditions (varying $\varepsilon$ by one order of magnitude results in ring density variations that are within the standard error reported here). The results are shown in Table I. [22]

| Ring     | Normalized Density |
|----------|--------------------|
| 1st      | 3.15 ± 0.04        |
| 2nd      | 1.40 ± 0.07        |
| Bulk core| 1.01 ± 0.02        |

TABLE I. Densities of each ring, calculated from MD simulation, normalized by the reservoir density.

Combining the predicted locations and widths for the rings with the ring densities calculated from MD simulation, we can construct the following expression for the overall normalized density as a function of CNT radius $R$:

$$\rho(R) = \frac{1}{R^2} \left( (r_{1,\text{out}}^2 - r_{1,\text{in}}^2) 3.15 + (r_{2,\text{out}}^2 - r_{2,\text{in}}^2) 1.40 + r_{3,\text{out}}^2 \right).$$

(7)

It can be shown that this expression asymptotically approaches unity for large $R$, as expected. Here it is important to recall that this density is normalized by the density of fluid molecules in the reservoir region ($\rho_{\text{bulk}}$).

The close agreement between (7) and the actual densities measured in MD simulations is shown in Fig. 5 for a reservoir density of $1.0 \sigma_f^{-3}$. For $R > 15\text{Å}$, the discrepancy is within 3% for all simulated CNTs.

Extensions to Nanoconfined Water: In the most common water models for MD simulations (e.g. SPC/E [23], TIP3P [24], TIP4P [25]), the interaction between the oxygen atom and other atoms is described by an LJ potential. Since these models assume that LJ interactions between hydrogen and carbon are negligible compared to LJ interactions between oxygen and carbon, we can use the previously described method to predict the root of the oxygen radial distribution function (RDF) for water confined within a CNT. These predictions agree closely with results from 6 sets of MD simulations (Figure 6). This analytical prediction is a definite improvement over current approaches found in the literature, which rely on MD simulations [18, 20].
we also show that fluid densities within each ring are very nearly constant. Combining this knowledge about fluid structure and density in the first two rings provides a closed-form expression for the normalized density of a confined fluid as a function of CNT radius that is in excellent agreement with MD simulations. We also show that this theory can be used to predict the equilibrium properties of water confined within CNTs with good accuracy. A complete description of the anomalous density for water in CNTs will be discussed in the near future.

Despite the focus on equilibrium densities, the results discussed here are in fact useful for non-equilibrium situations involving fluid flow. For example, our results can be used to provide estimates for the true cross-sectional area of nanotubes for predicting the flow velocity enhancement downstream of a constriction [26]. We also note that it has been shown in MD simulations of water in CNTs that flow does not appreciably affect the water structure (e.g., oxygen and hydrogen RDFs) [19]. This suggests that the above results may also prove useful for developing models predicting water flow rates in CNTs.

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**Molecular Dynamics Simulations:** We simulated CNTs of radii ranging from 9 Å to 35 Å. All CNTs were of armchair chirality; it has been shown that chirality has no observable impact on equilibrium fluid density within a CNT [4]. The majority of simulations were conducted at 300 K in LAMMPS [28] in the NVT ensemble coupled to a Berendsen thermostat [29]; some simulations at 100 K and 400 K were performed to ensure no dependence of fluid structure on temperature. In each case, the CNT length was at least three times its radius to reduce end effects. Each CNT was placed in a fluid bath with periodic boundary conditions. The size of the bath was at least twice the size of the CNT in each dimension to ensure that the finite bath size did not affect simulation results. Simulations were performed for reservoir densities $\rho_{\text{bulk}} \in \{0.8\sigma_f^{-3}, 1.0\sigma_f^{-3}, 1.1\sigma_f^{-3}\}$.

Interactions between carbon and fluid molecules were modeled using $\sigma = 3.28$ Å and $\varepsilon = 0.48$ kJ mol$^{-1}$ and interactions between fluid molecules were modeled using $\sigma_f = 3.15$ Å and $\varepsilon = 0.64$ kJ mol$^{-1}$. These parameters correspond to interactions between carbon and monatomic oxygen [24] and were chosen with simulations of water in CNTs in mind. Simulations of water utilized the TIP4P potential [25] with the same LJ parameters governing oxygen-carbon interactions. The CNT was kept rigid throughout each simulation. The simulation time step was 2.0 fs. Each system was allowed to equilibrate for 2.0 ns, after which atom kinematics were recorded every 2.0 fs for a total of 5.0 ns. To facilitate convergence to equilibrium density, CNTs were pre-filled to a density of 0.2.

**FIG. 5.** Theoretical prediction for $\rho(R)$ with densities measured from MD simulations overlaid.

**FIG. 6.** Theoretical prediction for maximum accessible radius of the oxygen atom in a water molecule and maximum accessible radius from MD simulations by [4], [11], [19], [13], [27], and authors.
The hypergeometric function can be expanded, using a theorem due to Gauss, in the form
\[
F_{\alpha,\beta,\gamma}(\delta_{\text{max}}^2) = \frac{\Gamma(\gamma)\Gamma(\gamma - \alpha - \beta)}{\Gamma(\gamma - \alpha)\Gamma(\gamma - \beta)} \left( 1 + O\left( \frac{\sigma^2}{R^2} \right) \right)
\]