Fullerenes, Nanotubes and Carbon Nanostructures

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/lfnn20>

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Published online: 06 Nov 2007.

To cite this article: Ruzeng Zhu, Shuwen Cui, Hong Yan, Yuhua Wen & Quanwen Yang (2007) Tolman Effect on Fluid Dynamics in Carbon Nanotubes, *Fullerenes, Nanotubes and Carbon Nanostructures*, 15:6, 417-426, DOI: [10.1080/15363830701655747](https://doi.org/10.1080/15363830701655747)

To link to this article: <http://dx.doi.org/10.1080/15363830701655747>

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Abstract: The numerical solutions of $\sigma(R)$ given by two different methods (Samsonov et al., 2003; and Lu et al., 2005) are compared with the result that they are coincident closely (the difference is within 4%). We conclude that it is necessary to consider the Tolman correction in the calculation of fluid dynamics in carbon nanotubes. Although our conclusion is the same as that of Prylutsky et al. (2005), the sign of our Tolman correction is opposite to theirs, and the difference can be attributed to the errors appeared in the paper of Prylutsky et al.

Keywords: Tolman effect, carbon nanotubes, surface tension and pressure of water

1 INTRODUCTION

Since the discovery of carbon nanotubes (CNTs) by Iijima in 1991 (1), the field of the prospective applications is growing rapidly. CNTs possess an extremely high mechanical strength, so the conduits for fluid transport at near molecular length scales provided by combining them are attractive

Received 14 February 2007, Accepted 1 June 2007.

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candidates for implementation in future micro- or nanofluidic devices. Obviously, understanding fluid behavior in nanochannels is important for the proper design and efficient operation of such devices. Therefore, a new field of fluid dynamics, Nanofluidics, which deals with fluid (gas, liquid) flow around and/or inside nanoscale systems, has grown. In nanoconduit, surface or interface force is a dominant force relative to body force because of the large surface-area-to-volume ratio, making surface tension important for Nanofluidics. In addition, the surface tension behaves like a Tolman effect, that is, it changes with the phase interface curvature radius R (2) according to the equation

$$\frac{1}{\sigma} \frac{d\sigma}{dR} = \frac{[2\delta/R^2][1 + (\delta/R) + 1/3(\delta^2/R^2)]}{1 + [2\delta/R][1 + (\delta/R) + 1/3(\delta^2/R^2)]} \quad (1)$$

where σ is the surface tension of liquid, δ is Tolman length, the separation between the equimolar surface and the surface of tension, $\delta = R_e - R_s$. Neglecting the terms δ/R and $\delta^2/3R^2$ in comparison with unity, and treating δ as a constant, the integral of equation 1 can be readily evaluated to give the simple result

$$\sigma/\sigma_0 = 1/(1 + 2\delta/R) \quad (2)$$

where σ_0 is the surface tension of liquid for a flat surface. The first approximation of Equation 2

$$\sigma = \sigma_0 \left(1 - \frac{2\delta}{R} \right) \quad (3)$$

Although no significant change of surface tension can be expected for the fluid in a conduit of appreciable radii, we can expect very significant changes when we go to a conduit of smaller radii, down to one nanometer or less. Therefore for Nanofluidics, whether beside surface tension, its dependence on the curvature radii of the surface must also be considered as an important question.

In some experimental studies of capillary phenomena in carbon nanotubes, the nanotubes have been filled, at least partially, with molten metals, salts and oxides through capillary action (3–6), but little has been reported on the dynamic aspects of fluid transport during or after the CNT-filling process. The studies of fluid interface motion in nanochannels of multi-walled CNT (MWNT) were performed recently (7, 8) using a transmission electron microscope. Good wettability of the inner carbon walls by the water-based fluid was shown. Fully reversible interface dynamic phenomena were visualized, and an attempt was made to explain the origin of this fine-scale motion. Megaridis et al. (8) estimated the surface tension of water in the multi-walled CNT as $\sigma \sim 30\text{--}80 \text{ mN/m}$. Prylutskyy et al. (9) calculated and analyzed the surface tension and water pressure in carbon nanotubes with diameters of 0.4–1.0 nm in detail. However, the key

Equation (5')* in their paper is wrong, and so the surface tension and pressure of water in carbon nanotubes with diameters from 0.4 to 1.0 nm given by the calculation based on Equation (5') are also wrong. Therefore, their conclusion that "it is necessary to consider the Tolman correction (10) for calculating the surface tension and the pressure of liquid in subnanometer-diameter CNT," lost its basis and must be checked again (9).

In the present paper, we re-examine this question, that is, we calculate and analyze the surface tension and pressure of water in carbon nanotubes with diameters of 0.4–1.0 nm in detail on a correct base to see whether it is necessary to consider the Tolman correction (10) for calculating the surface tension and the pressure of liquid in carbon nanotubes. After doing so in section 2, a comment on Reference (9) is given in section 3.

2 ANALYSIS AND CALCULATION

If we define the Tolman length δ in equation 3 as a constant δ_∞ , then Equation (3) is applicable only under the condition $R_s \gg \delta_\infty$, where R_s refers to the radius of tension surface of a droplet. For water, some papers discussed the surface tension as a function of R_s' $\sigma(R_s)$ directly.

In 2003, Samsonov et al. (11), with the idea that free surface energy is the work done in cutting a massive phase into two half spaces, considered the process of separation (excision) of a spherical volume of radius R_e from a massive parent phase. In as much as the small radius R_e corresponds to the equimolecular separating surface, the specific free surface energy coincides with the surface tension $\sigma(R_e)$. They obtained the integral formula for $\sigma(R_e)$

$$\sigma(R_e) = -\frac{1}{16\pi R_e^2} n_1^2 \int dV_1 \int dV_2 g_0(r) \Phi(r) \quad (4)$$

where n_1 is the number of molecules per unit volume in the parent phase, and r is the distance between molecules. The volume V_2 is selected with regard to the range of action of the pair potential $\Phi(r)$. The unperturbed structure of the massive phase is described by the unperturbed binary correlative function $g_0(r_1, r_2)$, which coincides with the radial distribution function $g_0(r)$. The six-dimensional integral in Equation 4 was calculated based on the Monte Carlo method. On the one hand, numerical integration entails the appearance of some error (estimated to be no more than 5%). On the other hand, integration by the Monte Carlo method makes it possible to more adequately take into account correlations between two molecules, one with the center in volume V_1 and one with the center in volume V_2 . In analytical integration, a spherical layer with a thickness on the order of the

*The serial number of equation or figure with superscript (') is the one in Reference (9) with the same serial number but without superscript (').

effective molecular diameter should be excluded from consideration to avoid divergence.

The integral in Equation (4) is not structure-sensitive. Here, the radial distribution function $g_0(r)$ for a Lennard-Jones system was calculated by the Kirkwood method with the use of the expansion coefficients from (12). At the same time, they showed in (13) that the use of the simplest approximation

$$g_0(r) = \begin{cases} 0 & \text{at } r < a \\ 1 & \text{at } r \geq a \end{cases} \tag{5}$$

does not change the dependence of the reduced specific free surface energy $\sigma^* = \sigma/\sigma_0$ on the reduced radius of a small object $R^* = R/a$ (a is the effective molecular diameter, and σ_0 corresponds to a flat interface).

Figure 1 shows the plot of $\sigma(R_e)$ for water microdrops found by Samsonov et al. (11) with the use of the Stockmayer potential (14). It can be seen that at $R_e > 1$ nm the surface tension attains the asymptotic value of 70 mJ/m², which agrees with the experimental value (72 mJ/m²) (15). Some oscillations of the function $\sigma(R_e)$ seem to be a result of errors in calculation. In addition, Samsonov et al. calculated several other substances to prove the correctness of their theory.

Using Laplace equation

$$\Delta p = \frac{2\sigma}{R} \tag{6}$$

Figure 1. The plot of $\sigma_e(R)$ for water nanodrops at room temperature obtain by the approximation of computer-aided calculation (13).

and numerical solution $\sigma_e(R)$ shown in Figure 1, we have calculated the pressure of water in the SWNT as a function of its radius, with the results shown in Figure 3 (curve 3). In fact, the approximate theory of Samsonov et al. can't differentiate R_e from R_s . Therefore in Figure 3, the differences between (R_e, σ_e) and (R_s, σ_s) have been ignored so that they are represented by (R, σ) . It can be seen from Figure 3 that the δ changes with R .

On the other hand, in 2005, Lu et al. (16) extended the model for the size-dependent surface energy of solid $\sigma_{sv}(R)$ to determine the size-dependent surface tension $\sigma(R)$ of liquid droplets, free of any adjustable parameter. For a planar interface at the melting point, $\sigma_{sv0}/\sigma_0 = k$ for metallic elements with $k = 1.18 \pm 0.03$. Note that in the derivation of $\sigma_{sv}(R)$, it is assumed that the nanocrystal has the same structure as that of the corresponding bulk (17). The above expression for the bulk maybe extended to nanometer size with the same form

$$\frac{\sigma(R)}{\sigma_{sv}} = k \quad (7)$$

σ_{sv}/σ_{sv0} can be determined by (17)

$$\sigma_{sv}(R) = \sigma_{sv0} \left[1 - \frac{1}{4R/(h-1)} \right] \exp \left(-\frac{2S_b}{3R_{igc}} \frac{1}{4R/(h-1)} \right) \quad (8)$$

where h is the atomic diameter, where $S_b = E_0/T_b$ is the solid-vapor transition entropy of crystals with E_0 and T_b being the bulk solid-vapor transition enthalpy and temperature, respectively. R_{igc} is the ideal gas constant.

So they obtained the equation of $\sigma(R)$

$$\sigma(R) = \sigma_0 \left[1 - \frac{1}{4R/(h-1)} \right] \exp \left(-\frac{2S_b}{3R_{igc}} \frac{1}{4R/(h-1)} \right) \quad (9)$$

In terms of Equation (9), comparison of $\sigma(R)/\sigma_0$ for water between the model predictions and the computer simulation results is shown in Figure 2. The model prediction also corresponds to the computer simulation results. The definition for h in this case is defined as the O-H bond length. The parameters involved in Equation (9) are listed in Table 1.

It is observed that the plot in Figure 2 is consistent with statistical thermodynamics (18–20), computer simulations (21, 22) and other approaches (23) for Lennard-Jones fluids. In addition, Lu et al. (16) found reasonable agreements between the model predictions and those of computer simulations for other substances, for example, Na, Al. A comparison of Figures 1 and 2 illustrates that there is little difference between two plots of $\sigma(R)$, and $\sigma(R)$ decreases quickly with the decrease of size when $R \leq 0.5$ nm.

Using the data of Figure 2, we calculate the pressure of water in the SWNT as a function of its radius, which is shown in Figure 3 (curve 4). From Figure 3, it is seen that there is little difference between our curves 3 and 4, and Tolman correction into the pressure is approximately 25% at

Figure 2. R dependence of $\sigma(R)$ with $\delta = h$ for water (18).

$R = 0.4$ nm, 8% at $R = 0.7$ nm, and 5% at $R = 1.0$ nm. However, there is a distinct difference between ours and Prylutskyy's (curve 2), especially the signs of Tolman correction: Tolman correction of curves 3 and 4 is negative but positive for curve 2. The difference can be attributed to the errors that appeared in the paper of Prylutskyy et al., which will be discussed in section 3.

3 COMMENTS ON REFERENCE (9)

3.1 Main Equation (5') and Equation (7') are Wrong

3.1.1 The Deduction of Equation (5') is Wrong

In reference (9), the following imaginary experiment was made at $T = \text{const.}$ From a liquid, a spherical volume $V_0 = 4/3\pi R_0^3$ was set off. Afterward, this volume was extracted from the liquid and placed into saturated vapor. Under the action of surface tension forces, the drop diminished and took the

Table 1. Several necessary parameters used in the equations

	h (nm)	σ (mJ/m ²)	E_0 (kJ/mol)	T_b (K)	$S_b = E_0/T_b$ [J/(mol · K)]
H ₂ O	0.096	75	13.6	373	36.5

Figure 3. The calculated pressure of water in the CNT in dependence on their radii taking into account (curves 2, 3, 4) and without (curve 1) the Tolman correction.

volume $V = 4/3\pi R^3$ where R is the finite radius of the drop. Then the drop curvature radius reduction was introduced due to the surface tension $x = R_0 - R$. The following general isothermal equation of state was used for the liquid

$$\Delta p = p - p_0 = f\left(\frac{V_0 - V}{V_0}\right) = f\left(1 - \frac{1}{(1 + (x/R))^3}\right) \quad (2')$$

where the pressure p_0 and volume V_0 are the fiducial points laying on the coexistence curve. Combination of the equations

$$\Delta p = f(0) + 3f'(0)\frac{x}{R} + \frac{1}{2}(9f''(0) - 12f'(0))\left(\frac{x}{R}\right)^2 + \Lambda \quad (3')$$

$$\Delta p = \frac{2\sigma}{R} \quad (4')$$

and the first approximation of equation (2)

$$\sigma = \sigma_0\left(1 - \frac{2\delta}{R}\right) \quad (1')$$

give the following equation

$$\frac{2\sigma_0}{R}\left(1 - \frac{2\delta}{R}\right) = f(0) + 3f'(0)\left(\frac{x}{R}\right) + \frac{1}{2}(9f''(0) - 12f'(0))\left(\frac{x}{R}\right)^2 + \dots \quad (10)$$

and then making the coefficients of $(1/R)$ and $(1/R)^2$ on the left of equation (10) be equal to those on the right respectively to give

$$\delta = \frac{4f'(0) - 3f''(0)}{6(f'(0))^2} \sigma_0 \quad (5')$$

However, the latter step is not tenable. Because Equation (10) means that x is a function of R but not a constant, the present coefficients of $(1/R)$ and $(1/R)^2$ in Equation (10) are not the real ones. Therefore, we cannot make the present coefficients of $(1/R)$ and $(1/R)^2$ on the left of Equation (10) be equal to those on the right.

3.1.2 Equation (5') cannot Exist

Equation (10) alone cannot give Equation (5'). The reason is there are three unknown variables (δ , x , R) in Equation (10), but we only have one equation. In fact, we can give the value of δ arbitrarily in Equation (10); then Equation (10) means that R is an implicit function of x .

3.1.3 Equation (7') is Wrong

In Reference (9), the Tait equation was taken as an isothermal equation, which works well in the vicinity of the coexistence curve (24)

$$\Delta p = p - p_0 = (B + p_0) \left(\exp \frac{V_0 - V}{AV_0} - 1 \right) + \frac{NkT}{V} \frac{V_0 - V}{V_0} \quad (6')$$

where A and B are constants, N is the number of molecules, k is Boltzmann constant, p_0 is the pressure and V_0 is the volume.

Taking into account the Tait Equation of state (6') and the general expression to the Tolman correction (5'), they had

$$\delta = \frac{4(B + p_0)/A - 3(B + p_0)/A^2 - 2NkT/V_0}{6V_0^2(B + p_0)/AV_0 + NkT/V_0^2} \cdot \sigma_0 \quad (7')$$

Because Equation (7') is derived from the incorrect Equation (5'), it is also wrong.

3.2 The Mistake in the Comparison of Equation (5') with Experiment Data

For the aqueous solution under room temperature, Equation (7') gives Tolman length $\delta = -0.1$ nm, which is coincident with that estimated from experimental data $\delta_{\max} = -0.11$ nm. However, the estimation of the maximum Tolman length $\delta_{\max} = -0.11$ nm from Equation (1') with experimental data $\sigma_0 = 72$ mN/m (the surface tension of pure water at room temperature),

$\sigma_{\max} = 80$ mN/m, and $R_{\max} = 1$ nm is wrong, because the value of $R_{\max} = 1$ nm announced to be from Reference (8) is wrong. In fact, the real value of $R_{\max}$ given in Reference (8) is $R_{\max} = 50$ nm, which, along with the same data $\sigma_0 = 72$ mN/m, $\sigma_{\max} = 80$ mN/m as used in Reference (8), would give $\delta_{\max} = +2.78$ nm, not $\delta_{\max} = -0.11$ given by Equation (7').

Moreover, according to Reference (8) $\sigma_{\max} = 80$ mN/m is the upper limit of approximately experimental data. There is lower limit $\sigma_{\min} = 30$ mN/m in it as well. One could not relate $\sigma_{\max} = 80$ mN/m and $\sigma_0 = 72$ mN/m by Equation (1') directly.

3.3 The Pressure Shown in Figure 1' is Wrong

The plot of pressure in Figure 1' is wrong because it was computed from Equation (1') and (4') with the incorrect data $\delta = \delta_{\max} = -0.11$ nm. How big the error of Figure 1' has been discussed above.

4 CONCLUSIONS

In summary, we compare the results of $\sigma(R)$ given by two different methods (Samsonov et al. and Lu et al.) and find they are closely coincident. The surface tension and pressure of water in carbon nanotubes with diameters of 0.4–1.0 nm have been calculated and analyzed in detail on the basis of these numerical solutions of $\sigma(R)$. We conclude it is necessary to consider the Tolman correction in the calculation of fluid dynamics in carbon nanotubes. Although our conclusion is the same as that of Prylutskyy et al., the sign of our Tolman correction is opposite to theirs, and the difference is attributed to the errors appearing in the paper by Prylutskyy et al.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China under Grant No. 10472128, and the Knowledge Innovation Program of Chinese Academy of Sciences (No. KJCX2-SW-L2).

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