Nanocapillarity: wetting of carbon nanotubes.

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Introduction

It is well documented in the modern literature that the conventional laws of capillarity such as Laplace, Kelvin, and Young-Dupre equations are not adequate when applied to fluids confined by particulate and porous materials. Specifics of interactions of fluids with solid surfaces at the nanoscale are of special engineering importance in view of recent discovery of carbon nanotubes and rapidly growing research in fiber reinforced nanocomposites and other nanotechnologies [1, 2]. We develop a theory of wetting of nanofibers with taking into account the effects of solid surface curvature and liquid-solid apolar and polar interactions [3]. It is shown that a transition from partial wetting to non-wetting may occur as the fiber diameter decreases. In particular, contact angles of water on hydrophobic carbon fibers may vary from 75° (plane graphite surface) to 100-130° (carbon nanotubes).

Method

Conditions of thermodynamic equilibrium and stability of thin liquid films on curved solid surfaces are determined by a competition between capillarity and adhesion forces. The convex surfaces of fibers imply positive curvatures of coating liquid films and, therefore, a positive Laplace pressure, P_c, acting on the film-air surface, which tends to squeeze the liquid out of the film. Adhesion is a stabilizing factor. When the film-solid attractions dominates the surface-tension forces, films are stable. The film-solid interactions are accounted for in terms of the disjoining pressure, $\Pi(h)$ [4]. The equilibrium liquid configurations are observed when these forces are in balance. This means that in the absence of external forces, the Laplace pressure and the disjoining pressure may vary along the equilibrium film surface due to variations in the film thickness and substrate curvature; however, their sum must be constant:

$$P_{cap} = P_l - P_g = \gamma\left(\frac{1}{R_1} + \frac{1}{R_2}\right) - \Pi(h) \qquad (1)$$

Here, γ is the liquid surface tension, R_1 and R_2 are the two principal radii of curvature of the outer surface of the film. The capillary pressure, P_{cap}, is the difference between the liquid pressure, P_l, and the gas pressure, P_g, and is, therefore, positive for films on convex surfaces of fibers. Eq.1 for mechanical equilibrium of the liquid layer of varying thickness (droplet passing into film) can be expressed as a second order differential equation with regard to the layer thickness $h(z)$:

$$\gamma\left[-\frac{h''}{\left(1+h'^2\right)^{3/2}} + \frac{1}{(a+h)\left(1+h'^2\right)^{1/2}}\right] = P_{cap} + \Pi(h) \qquad (2)$$

Solution of Eq.2 with the corresponding boundary conditions gives the equilibrium profile of the droplet and transition zone between the droplet and the film.

As one of the analytical results following from Eq.2 we have obtained a relation between the apparent contact angle formed by droplets on fibers and the disjoining pressure integral:

$$\cos\theta = 1 + \frac{1}{\gamma(a+h_\infty)}\int_{h_\infty}^{h_0}(a+h)\Pi(h)dh \qquad (3)$$

Here, a is the fiber radius and h_∞ is the equilibrium film thickness which in its turn depends on the fiber radius and disjoining pressure. In the limit $a \to \infty$, Eq.3 reduces to the Frumkin-Derjaguin equation for wetting of plane surfaces [4].

In general, the disjoining pressure, $\Pi(h)$, can be represented as a sum of the long range apolar (dispersion) and short range polar (e.g., acid-base) components [4,5]:

$$\Pi(h) = 2d_0^2 S_d / h^3 + S_p l_0^{-1}\exp\left((d_0 - h)/l_0\right) \qquad (4)$$

Here, d_0 is a lower cut-off distance of fluid-solid intermolecular forces where the Born repulsion may be replaced by the hard wall (vertical rise in the potential to infinity prohibiting overlap of fluid and solid molecules). d_0 is a molecular scale of the order of 0.1-0.2 nm. S_d and S_p are the apolar and polar components of spreading coefficient, S. For wetting liquids $S_d > 0$, and the dispersion component of disjoining pressure (4)

is positive. The polar component of disjoining pressure is assumed to decay exponentially with a correlation length, l_0 [4,5]. The correlation length for water interaction with solid substrates is of the order of 0.6 nm and even larger [5]. Spreading coefficients, S_d and S_p, for a particular liquid-solid pair can be calculated from the apolar and polar components of the liquid and solid surface tensions and the contact angle on a plane solid [5]. Spreading coefficients, S_d and S_p, may be positive or negative depending on the system.

Results and Discussion

In Fig.1 and 2 we present examples of the estimates of the apparent contact angles on carbon nanotubes. The outer surface of carbon nanotubes is regarded as graphite-like [1,2]; therefore for modeling interaction of fluids with nanotubes it is justified to use intermolecular potentials in the form of Eq.4 introduced in the literature to model graphite surfaces [6].
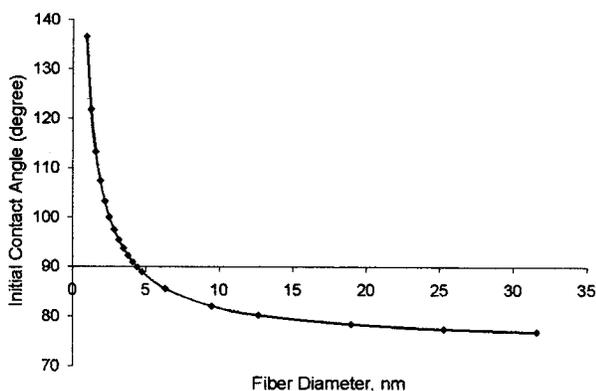

Fig. 1. Dependence of the initial contact angle on the fiber diameter. Wetting of dry carbon nanotubes with graphite-like surface characterized by the parameters [6]: $\lambda_d = S_d / \gamma$ =1.468, l_0/d_0=3.8, d_0=0.158 nm.

These parameters refer to partial wetting of the dry graphite surface with the initial contact angle 75^0 and the equilibrium contact angle 109°. Transition from partial wetting of dry surface to non-wetting (90° initial contact angle) is observed at the fiber diameter $2a$=4.1nm.
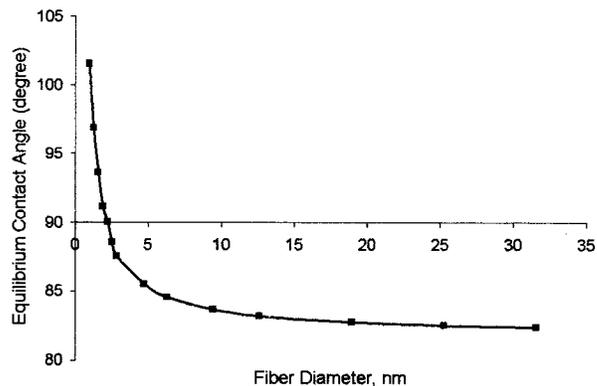

Fig. 2. Dependence of the equilibrium contact angle on the fiber diameter. Equilibrium wetting of carbon nanobutes with graphite-like surface characterized by the initial contact angle 75° and the equilibrium contact angle 82°, $\lambda_d = S_d / \gamma$ =0.5, l_0/d_0=3.8, d_0=0.158 nm.

In this case transition from partial wetting to non-wetting (90° contact angle) is observed at the fiber diameter $2a$=2.2 nm.

Conclusions

A theory of wetting of nanofibers has been developed with taking into account the effects of solid surface curvature and liquid-solid apolar and polar interactions The estimates presented confirm our main conclusion: liquids which wet graphite surfaces would not necessarily wet carbon nanotubes. The fiber curvature has to be considered as an important factor affecting fiber wettability. As the fiber diameter decreases the apparent contact angle increases and can exceed 90° that corresponds to the transition from wetting and non-wetting.

References

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