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An analogy between the adhesion of liquid drops and single-walled nanotubes

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This paper establishes an analogy between the adhesion of liquid drops and single-walled nanotubes. Carbon nanotubes are found to be "super-hydrophobic" for radii smaller than ~6 Å, whereas the "hydrophobic/hydrophilic" transition takes place at a radius of ~16 Å. The liquid drop analogy provides simple laws for treating the complex problem of the adhesion of highly deformed single-walled nanotubes. We compare our findings with atomistic or continuum simulations and elastica solutions, finding a relevant agreement.

Keywords: Wetting; Carbon and graphite; Nanostructure; Analytical methods

The adhesion of liquid drops, reviewed notably by Quèrè [1] is a fascinating field, some two hundred years old, and could present analogies with the adhesion of single-walled nanotubes, recently theoretically investigated by Tang et al. [2]. Continuum [3] or atomistic [2,4] simulations have confirmed the complex behaviour involved in the adhesion of single-walled nanotubes, mainly due to the inevitable presence of large displacements, deformations and contacts. Such adhesion is therefore outside the domain of linear elasticity and falls under the elastica theory of shells, for which only numerical integrations can be obtained [2]. Self-collapsed configurations have also been numerically computed [3,5]. Adhesion between nanotubes is imposed by van der Waals attraction and, due to the tremendous surface to volume ratio [6] of nano-objects, becomes predominant at the nanoscale. Geckos and spiders take advantage of this, but nanoscale adhesion could pose limitations to the range of applicability of nano-systems. Such reasons have motivated the present study, with the aim of providing simple laws for treating this complex phenomenon.

The adhesion of a small (i.e. one for which surface tension prevails over gravity) liquid drop is fully described by the contact angle θ (a function of the liquid/solid/vapour surface energies) between drop and substrate: see Figure 1a (with $r = 0$). With R_0 the radius of the drop in air and R the radius of curvature of the spherical cap describing the adhering drop, the radius of the contact area a can be calculated assuming mass conservation. The adhesion between single-walled nanotubes of radius R_0 can be similarly described by the contact angle θ (which we expect to be a function of the adhesion work and bending stiffness), the radius of curvature R of the deformed non-contact segment, the radius of curvature r of the blunt notches (that, as a first approximation, could be assumed to be zero, as for a liquid drop) and the contact half-length $a = (R - r)\sin\theta$ (see Fig. 1a). The nanotube mass conservation basically imposes its inextensible condition, i.e. $a + (\pi - \theta)r + R\theta = \pi R_0$ (Fig. 1a). Accordingly we deduce:

$$\frac{a}{\pi R_0} = \frac{1 - r/R_0}{1 + \theta/\sin\theta}. \tag{1}$$

For small contacts $\theta \to \pi$ and $a/(\pi R_0) \approx (1 - r/R_0)\sin\theta/\theta$. This asymptotic solution in the limit of $r/R_0 \to 0$ can be directly compared with the analytical result reported in Ref. [2]; thus, we can define the contact angle for a single-walled nanotube, having Young's modulus E, Poisson's ratio v, thickness t and contact surface energy γ_S (here due to van der Waals attraction):

$$\frac{\sin\theta}{\theta} = 1 - \frac{R_0^*}{R_0}; \quad R_0^* = \sqrt{\frac{D}{2\gamma_S}}, \quad D = \frac{Et^3}{12(1 - v^2)}, \tag{2}$$

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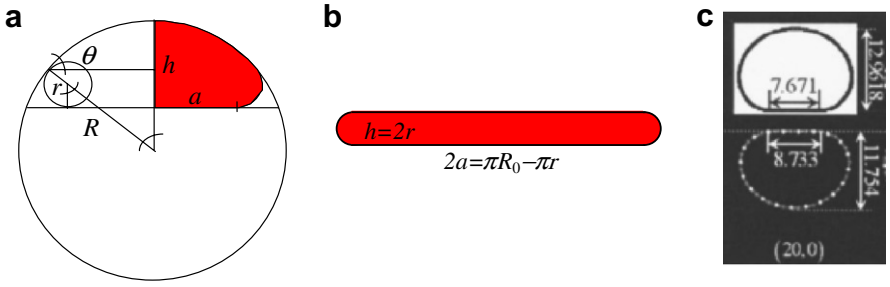
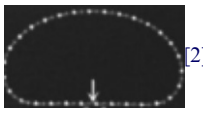
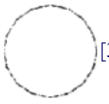
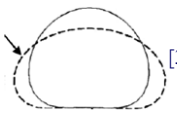
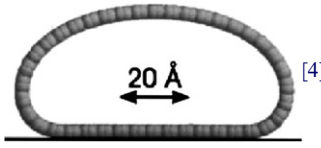
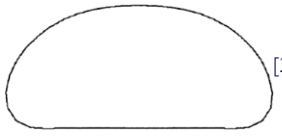


Figure 1. Single-walled nanotube (liquid drop) geometry, under large contact/deformation (a), squashed configuration (b), and continuum (up) or atomistic (down) computed shapes for a (20,0) carbon nanotube [3].

where D is the nanotube bending stiffness, as imposed by the shell model. Thus the contact will be "hydrophobic" ($\theta > \pi/2$, water/nanotube repellent) or "hydrophilic" ($\theta < \pi/2$) for $R_0 < R_0^{/}$ or $R_0 > R_0^{/}$ with $R_0^{/} = \pi R_0^*/(\pi - 2) \approx 2.75 R_0^*$ (e.g. $R_0^{/} \approx 16.5$ Å for $R_0^* \approx 6$ Å) and "super-hydrophobic/hydrophilic" ($\theta \approx \pi,0$) for $R_0 \approx R_0^*$ or $R_0 \gg R_0^{/}$. A "super-hydrophobic" nanotube would have interesting properties, e.g. vanishing rolling friction, ideal for nano-rolling bearings. In fact Eq. (2) implies that the contact area is zero ($\theta = \pi$) for $R_0 \leqslant R_0^*$, as emphasized in Ref. [2]. Thus R_0^* represents a minimum radius, which gives an estimation of the

Table 1. Adhesion of single-walled carbon nanotubes (SWCNTs): shapes computed by atomistic [2,4] or continuum simulations [3] and prediction according to the present drop analogy, simply assuming $r = 0$ and $R_0^* \approx 6$ Å ($D = 1.44 \times 10^{-19}$ Nm, $2\gamma_S = 0.40$ J/m^2)

SWCNTs	R_0 [Å]	Computed shapes (reference)	θ [°]	$\frac{R}{R_0}$	$\frac{\Phi}{10^{-10}\ \mathrm{J/m}}$	$\frac{a}{\pi R_0}$	$\frac{h}{2R_0}$
(10,0)	3.915	 [2]	180.00	1.00	0.00	0.00	1.00
(12,0)	4.698	 [2]	180.00	1.00	0.00	0.00	1.00
(30,0)	11.745	 [2]	110.01	1.10	4.95	0.33	0.74
(10,10)	6.781	 [4]	161.00	1.00	1.55	0.10	0.97
(10,10)	6.781	 [3]	161.00	1.00	1.55	0.10	0.97
(20,20)	13.562	 [4]	100.84	1.15	5.40	0.36	0.68
(20,20)	13.562	 [3]	100.84	1.15	5.40	0.36	0.68
(40,40)	27.127	 [4]	68.18	1.48	6.60	0.44	0.46
(40,40)	27.127	 [3]	68.18	1.48	6.60	0.44	0.46

Nanotube (40,40) is the only "hydrophilic" one.

radius r of the blunt notches (and thus, in our treatment, $0 \leqslant r/R_0, R_0^*/R_0 \leqslant 1$).

Introducing Eq. (2) into Eq. (1) we find the following nonlinear law:

$$\frac{a}{\pi R_0} = \frac{(1 - R_0^*/R_0)(1 - r/R_0)}{2 - R_0^*/R_0}. \tag{3}$$

For small contacts/deformations ($\theta \to \pi$ or $R_0^*/R_0 \to 1$) and vanishing blunt radius ($r/R_0 \to 0$) the prediction of Eq. (3) is identical to the asymptotic solution reported in Ref. [2], whereas for large contacts/deformations ($\theta \to 0$ or $R_0^*/R_0 \to 0$) $a/(\pi R_0) = (1 - r/R_0)/2$, as coherently imposed by the inextensible condition (see Fig. 1b). However, note that in the limit of small contacts/deformations and non-vanishing blunt radius our prediction is slightly different from that reported in Ref. [2]; for example for $r = R_0^*$, $a/(\pi R_0) = (1 - R_0^*/R_0)^\alpha$ with $\alpha = 2$, whereas in Ref. [2] $\alpha = 1$.

The (maximum) height of the flattened nanotube can be geometrically derived as (Fig. 1a):

$$\frac{h}{2R_0} = \frac{R + r}{2R_0} - \frac{R - r}{2R_0}\cos\theta, \quad \frac{R}{\pi R_0} = \frac{1 - \frac{a}{\pi R_0} - \frac{\pi - \theta}{\pi}\frac{r}{R_0}}{\theta}, \tag{4}$$

where θ is defined in Eq. (2). For $\theta \to 0$, $h,/(2R_0) \to r/R_0$ as coherently imposed by the inextensible condition (see Fig. 1b), whereas for $\theta \to \pi$, $h,/(2R_0) \to 1$.

During the loss of adhesion, the classical fracture mechanics energy balance must hold. Accordingly, the opposite of the variation of the total potential energy (elastic energy minus external work) with respect to the crack surface area (complementary to the contact area) must be equal to the work of adhesion $2\gamma_S$ (see Refs. [7,8]). Thus $\mathrm{d}\Phi = 4\gamma_S \mathrm{d}a$ (the external work is here zero), where Φ denotes the elastic energy per unit length stored in the nanotube. By integration, following Ref. [9], we can calculate the energy stored in the largely deformed nanotube:

$$\Phi = 4\gamma_S a = 4\pi R_0 \gamma_S \frac{(1 - R_0^*/R_0)(1 - r/R_0)}{2 - R_0^*/R_0}. \tag{5}$$

Let us consider the numerical example investigated in Ref. [2], as shown in Figure 1c (adapted from Ref. [2]). Note the similarity between the deformed shapes of a nanotube and a drop. For the investigated (20,0) nanotube ($R_0 = 7.83$ Å) the size of the contact calculated [2] by molecular simulations is $2a = 8.73$ Å, with a flattened nanotube height equal to $h = 11.75$ Å (Fig. 1c). Such values are comparable with those obtained by numerically integrating the elastica differential equation, which yields [2] $2a = 7.67$ Å and $h = 12.96$ Å (Fig. 1c). The critical radius R_0^* must be around 5 Å, as reported in Ref. [2] ($R_0^* \approx 4.77$ Å) or as suggested by the shape of self-collapsed nanotubes [3] ($R_0^* \approx r \approx 5.5$ Å). Note that, taking the theoretical value of $2\gamma_S = 0.40\ \mathrm{J/m^2}$, $R_0^* \approx 4.77$ Å would correspond to $D = 0.91 \times 10^{-19}$ Nm, whereas $R_0^* \approx 5.5$ Å to $D = 1.21 \times 10^{-19}$ Nm (in Ref. [3] values from the literature between $D = 1.37 \times 10^{-19}$ Nm and $D = 2.35 \times 10^{-19}$ Nm are reported, whereas in Ref. [2] slightly smaller values, as emphasized by the same authors, were calculated). We consider the two limiting hypotheses of $r = 0$ or $r = R_0^*$. For $r = 0$ and $R_0^* \approx 6$ Å we deduce plausible values of $2a = 9.32$ Å and $h = 14.35$ Å ($\theta = 2.51$ radians, i.e. 143.81°, thus this nanotube is "hydrophobic"; the deformed radius is $R = 7.94$ Å and the computed elastic energy per unit length is $\Phi = 3.73 \times 10^{-10}$ J/m). Alternatively, for $r = R_0^*$ and $R_0^* \approx 4$ Å we again deduce plausible values of $2a = 7.90$ Å and $h = 13.65$ Å ($\theta = 1.92$ radians, i.e. 110.01°, $R = 8.21$ Å, $\Phi = 3.16 \times 10^{-10}$ J/m). Fitting independently r and R_0^* we could identically match the atomistic simulation results for both a and h. We further compare our approach with additional deformed nanotube shapes computed according to atomistic [2,4] or continuum [3] simulations: the results are reported and discussed in Table 1. In these cases too a good agreement is found.

We conclude that our liquid drop analogy could be useful in treating with simple laws, i.e. Eqs. (1)–(5), the complex problem of the adhesion of largely deformed single-walled nanotubes e.g. in nanovector therapeutics.

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