

Breakdown in the Wetting Transparency of Graphene

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We develop a theory to model the van der Waals interactions between liquid and graphene, including quantifying the wetting behavior of a graphene-coated surface. Molecular dynamics simulations and contact angle measurements were also carried out to test the theory. We show that graphene is only partially transparent to wetting and that the predicted highest attainable contact angle of water on a graphene-coated surface is 96°. Our findings reveal a more complex picture of wetting on graphene than what has been reported recently as complete “wetting transparency.”

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Graphene, a sheet consisting of a single-layer sp^2 lattice of carbon [1], combines optical transparency, electrical conductivity, and mechanical strength [2–6]. The production of large-area graphene [7] using chemical vapor deposition (CVD) has further shed light on engineering the material for real applications. Despite active research to demonstrate the unique electronic and mechanical properties of graphene, only a few reports [8–11] have studied the interfacial behavior between graphene and liquid, including the wetting properties of graphene. Very recently, Rafiee *et al.* [11] reported the “wetting transparency” of graphene, which suggests that the van der Waals (vdW) interactions between graphene and any liquid placed on top are negligible, allowing the “transmission” of the substrate contact angle to fluid above graphene. The wetting transparency implies that (i) monolayer graphene itself is a “superomniphobic” material [12], where the contact angle θ of any liquid droplet on a suspended monolayer graphene should approach 180°, and (ii) any surface can become electrically conductive without affecting its inherent wetting behavior by coating it with a monolayer graphene film. Clearly, implications (i) and (ii) above could represent breakthroughs in the field of wetting. However, the experimental evidence presented in Ref. [11] is not sufficient to support the complete “transparency” of graphene to wetting, because Ref. [11] considered only systems exhibiting a restricted range of contact angles ($30^\circ < \theta < 90^\circ$). A more complete study and analysis are required to elucidate the wetting behavior of graphene, including the role of the underlying solid substrates.

In this Letter, we develop the first theory to properly model the vdW interactions between any liquid and a sheet of N -layer graphene. Since the contact angle of water on graphite ($N \rightarrow \infty$) is known experimentally [13], we are able to predict the contact angle of water on a suspended monolayer graphene ($N = 1$). Note that this predicted contact angle represents the upper limit of contact angles attainable for a water droplet on a graphene-coated surface.

To test the theory, we considered water on a sheet of suspended monolayer graphene and carried out molecular dynamics (MD) simulations to determine the contact angle corresponding to an infinitely large water droplet, θ_∞ [14]. Using the theory, we also obtained an expression for the vdW interactions between liquid and a sheet of N -layer graphene supported by a solid substrate. Through a comparison with the calculated contact angles on bare solid surfaces, we show that graphene is not entirely transparent to wetting. Although the wetting behavior of the substrate does get partially transmitted through a sheet of monolayer graphene, the wetting transparency breaks down significantly on superhydrophobic and superhydrophilic substrates. Finally, we carried out contact angle measurements of water on CVD-grown graphene supported by hydrophobic and hydrophilic substrates to further validate our theory.

First, we model the vdW interactions between liquid and a sheet of N -layer graphene. The general expression for the attractive vdW interaction potential between one carbon atom in graphene and one liquid molecule, V_{CL} , is given by [15]

$$V_{CL} = \frac{-A_{CL}}{r^6}, \quad (1)$$

where r is the distance between the two entities considered and A_{CL} is the vdW interaction parameter between one carbon atom and one liquid molecule. Under the assumptions that (i) the vdW interaction dominates the interactions between graphene and liquid, (ii) A_{CL} is constant and independent of the number of stacking layers of graphene, and (iii) the vdW interactions are perfectly additive, the vdW interaction potential between one liquid molecule and a flat, infinitely large monolayer graphene sheet, w_{GL} , is given by

$$w_{GL}(z) = \sigma \int V_{CL} d\Sigma = \frac{-\pi\sigma A_{CL}}{2z^4}, \quad (2)$$

where (i) σ is the surface density of carbon atoms, which is assumed to be uniform with $\sigma = 4/(\sqrt{3}a^2)$, where $a = 2.49 \text{ \AA}$ is the graphene lattice constant [16], (ii) z is the

shortest distance between the liquid molecule and the graphene plane, and (iii) $d\Sigma$ is the differential surface area. By using Eq. (2), and assuming additivity of the vdW interaction potential, the vdW interaction potential between one liquid molecule and a flat, infinitely large N -layer graphene sheet, w_{NL} , is given by

$$w_{NL}(z) = \frac{-\pi\sigma A_{CL}}{2} \sum_{i=1}^N \frac{1}{[z + (i-1)d_0]^4}, \quad (3)$$

where d_0 is the interlayer distance between the graphitic planes in graphene (3.35 Å) [17]. We next assume that the density profile of liquid molecules as a function of z , $\rho_L(z)$, satisfies the Boltzmann distribution, that is [15],

$$\rho_L(z) = \rho_{L0} \exp[-w(z)/k_B T], \quad (4)$$

where ρ_{L0} is the number density of bulk liquid, w is the vdW interaction potential energy between one liquid molecule at z and the entire substrate, k_B is the Boltzmann constant, and T is the absolute temperature. Note that Eq. (4) does not consider the effect of short-range ordering of liquid molecules adjacent to the solid-liquid interface [15], which would introduce an additional parameter associated with the packing of liquid molecules. Note, however, that use of Eq. (4) improves upon the conventional constant liquid density assumption.

For a liquid droplet placed on a flat, infinitely large monolayer graphene sheet, $w(z)$ in Eq. (4) corresponds to $w_{GL}(z)$, and the total vdW interaction potential per unit area between liquid and a contacting monolayer graphene, Φ_{GL} , is given by

$$\Phi_{GL} = \int_{\delta_{GL}}^{\infty} \rho_{GL}(z) w_{GL}(z) dz, \quad (5)$$

where $\rho_{GL}(z) = \rho_{L0} \exp[-w_{GL}(z)/k_B T]$ and δ_{GL} is the equilibrium contact separation between the liquid and graphene. Similarly, the vdW interaction potential per unit area between liquid and a contacting N -layer graphene, Φ_{NL} , is given by

$$\Phi_{NL} = \sum_{i=1}^N \left[\int_{\delta_{GL} + (i-1)d_0}^{\infty} \rho_{NL}(z) w_{GL}(z) dz \right], \quad (6)$$

where $\rho_{NL}(z) = \rho_{L0} \exp[-w_{NL}(z)/k_B T]$ and we assume that δ_{GL} is independent of N . In general, the modified Young-Dupré equation is given by [18,19]

$$\gamma_L(1 + \cos\theta) = -\Phi, \quad (7)$$

where γ_L is the surface tension of the liquid and Φ is the vdW interaction potential per unit area between liquid and the entire substrate. By using Eqs. (3), (6), and (7), the contact angle of liquid on a sheet of suspended N -layer graphene can be calculated numerically.

Consider a water (w) droplet on a sheet of N -layer graphene at room temperature ($T = 298$ K), where δ_{GL} ($L = w$) is found to be 3.28 Å by using MD simulations [20]. The parameter A_{CL} , associated with the vdW interactions between water and graphene, can be

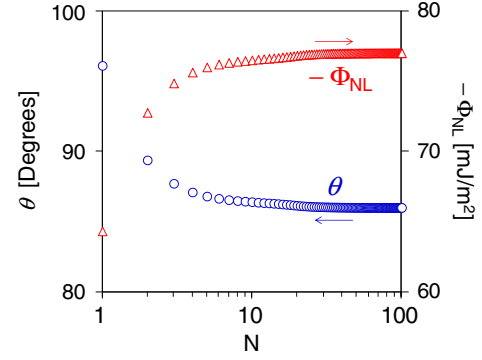


FIG. 1 (color online). Calculated $-\Phi_{NL}$ and the corresponding contact angle θ as a function of N on a suspended N -layer graphene.

determined by fitting the calculated contact angle of water on graphite ($N \rightarrow \infty$) to the experimental value (86° [13]). The deduced value of $A_{CL} = 8.914 \text{ eV } \text{\AA}^6$ was used in all the calculations that follow. The resulting $-\Phi_{NL}$ and θ , calculated by using Eqs. (6) and (7) for water placed on contacting a sheet of N -layer graphene as a function of the graphene layer number N , are shown in Fig. 1. Figure 1 shows that $-\Phi_{NL}$ between water ($L = w$) and graphite ($N \rightarrow \infty$) is 77 mJ/m^2 , which is slightly higher than the surface tension of water ($\gamma_L = 72.8 \text{ mJ/m}^2$ [15]). In addition, $-\Phi_{NL}$ decreases more rapidly when $N < 10$ due to the elimination of closer graphitic planes, and, therefore, the contact angle of water increases. For suspended monolayer graphene ($N = 1$), the calculated $-\Phi_{GL}$ is 64 mJ/m^2 , which is only 16% lower than that of water on graphite. The resulting contact angle for water on suspended monolayer graphene is only 96° , a value that is significantly lower than that corresponding to wetting transparency or superomniphobicity. Furthermore, under the assumption that the vdW interactions dominate the interactions between the liquid and the solid surface (for example, the electrostatic interactions induced by an electric field in electrowetting phenomena are not considered here), because adding an underlying solid substrate can only increase the value of $-\Phi$ in Eq. (7), the predicted 96° contact angle is the highest attainable one on a graphene-coated surface.

In order to test the calculated upper limit of the contact angle, we carried out MD simulations considering one nanodroplet of water on a flat, fixed, and suspended monolayer graphene under the NVT ensemble using the GROMACS 4.0 [21] software package. All the carbon atoms in graphene were treated as uncharged Lennard-Jones spheres using the force-field parameters reported by Tummala and Striolo [22]. The water molecules were simulated by using the extended simple point charge model [23]. The bond lengths for water molecules during simulations were constrained by using the SETTLE algorithm [24]. The vdW interactions were treated with a cutoff distance of 0.9 nm. Long-range

electrostatic interactions were treated by using the particle-mesh Ewald summation method [25]. The equations of motion were integrated with a time step of 2 fs using the Verlet algorithm [26]. The velocity-rescaled Berendsen thermostat was implemented to maintain the system at a constant temperature of 298 K [27].

It is noteworthy that current MD simulations can consider only a liquid droplet having nanometer size, for which the Young equation is not perfectly valid [28]. To calibrate the simulated contact angle, later studies [29–31] have attributed all the factors that result in a deviation from the Young equation to the effect of the line tension. Specifically, one can show that [32]

$$\cos\theta = \cos\theta_\infty - \frac{\tau}{\gamma_L R_{CL}}, \quad (8)$$

where θ_∞ is the contact angle corresponding to an infinitely large droplet, R_{CL} is the radius of the circular contact line of the droplet, and τ is the free-energy contribution due to the line tension. Note that, although one should expect a positive line tension, the τ value deduced from the MD simulated contact angles is usually negative [14]. In order to obtain θ_∞ , nanodroplets containing 250, 500, 1000, 2000, and 4000 water molecules were simulated. We found that the simulated contact angle takes longer to reach equilibrium as the droplet size increases. For example, the largest droplet considered here (4000 water molecules) took 100 ns to reach equilibrium, and a representative simulation snapshot is shown in Fig. 2(a). For each system simulated, the droplet radius profile as a function of z (where $z = 0$ denotes the location of the graphene surface), $R(z)$, was obtained by averaging 1000 postequilibrium configurations, which corresponds to 10 ns of simulation time, as shown in Fig. 2(b). The contact angle was subsequently extracted from the simulated $R(z)$ profile by using the algorithm proposed by Ingebrigtsen and Toxvaerd [14]. Figure 2(c) shows that the calculated $\cos\theta$ as a function of $(1/R_{CL})$, where $R_{CL} = R(\delta_{GL})$, satisfies Eq. (8). The calculated value of τ is -3.07×10^{-8} mJ/m, and the extrapolated θ_∞ , which corresponds to $1/R_{CL} = 0$, is 104° . Considering that the force-field parameters were not optimized, we believe that the obtained value of θ_∞ is reasonable and further confirms that monolayer graphene itself is not transparent to wetting.

Next, we consider the vdW interactions between liquid and a sheet of N -layer graphene supported by a solid substrate. We treat the solid substrate as a semi-infinite block having constant density ρ_S . Similar to the analyses presented above, the expression for the attractive vdW interaction potential between one solid atom and one liquid molecule, V_{SL} , is given by

$$V_{SL} = \frac{-A_{SL}}{r^6}, \quad (9)$$

where A_{SL} is the vdW interaction parameter between one solid atom and one liquid molecule. The vdW interaction

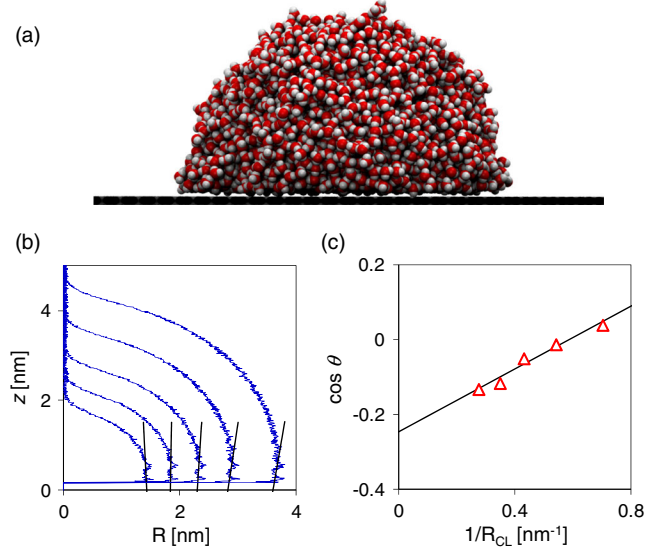


FIG. 2 (color online). (a) Postequilibrium MD simulation snapshot of a water droplet containing 4000 molecules on a sheet of flat, fixed, suspended monolayer graphene. Color code: Red, oxygen; white, hydrogen; and gray, carbon. (b) Simulated profiles for droplets with different sizes on the monolayer graphene. (c) Simulated $\cos\theta$ as a function of $1/R_{CL}$.

potential between one liquid molecule and the entire solid substrate considered, w_{SL} , is given by

$$w_{SL}(z) = \rho_S \int_z^\infty \left(\int V_{SL} d\Sigma \right) d\zeta = \frac{-\pi\rho_S A_{SL}}{6z^3}, \quad (10)$$

where z is the shortest distance from the liquid molecule to the solid surface and ζ is the coordinate variable along this direction. For a liquid droplet on the bare solid, the total vdW interaction potential per unit area between the liquid and the solid block, Φ_{SL} , is given by

$$\Phi_{SL} = \int_{\delta_{SL}}^\infty \rho_{SL}(z) w_{SL}(z) dz, \quad (11)$$

where $\rho_{SL}(z) = \rho_{L0} \exp[-w_{SL}(z)/k_B T]$ and δ_{SL} is the equilibrium contact separation between liquid and solid. Finally, for a liquid droplet on a sheet of N -layer graphene supported by a solid substrate, the total vdW interaction potential per unit area between liquid and the entire surface, Φ_{SNL} , is given by

$$\Phi_{SNL} = \sum_{i=1}^N \left[\int_{\delta_{GL} + (i-1)d_0}^\infty \rho_{SNL}(z) w_{GL}(z) dz \right] + \int_{\delta_{SNL}}^\infty \rho_{SNL}(z) w_{SL}(z) dz, \quad (12)$$

where $\rho_{SNL}(z) = \rho_{L0} \exp[-w_{SNL}(z)/k_B T]$, $w_{SNL}(z) = w_{NL}(z) + w_{SL}(z)$, and $\delta_{SNL} = \delta_{GL} + (N-1)d_0 + \delta_{SG}$, where δ_{SG} is the equilibrium contact separation between graphene and the solid. By using Eqs. (3), (6), (7), and (10)–(12), the contact angles of liquid on (i) a bare

solid substrate θ_S and (ii) a sheet of N -layer graphene supported by the solid substrate, θ_{GS} , can be calculated numerically.

In order to further elucidate the role of the underlying substrate on the contact angle of a liquid on graphene, we consider next the wetting of water on a solid substrate with and without a sheet of monolayer graphene ($N = 1$) between them. For water on the bare solid, we assume a constant value of $\delta_{SL} = 5 \text{ \AA}$, which is a reasonable contact distance between solid and liquid [15], and, by gradually increasing the value of $(\rho_S A_{SL})$ [see Eq. (10)] from 0 to 25 eV \AA^3 , the contact angle of water on the bare solid, denoted as θ_S , can be “artificially tuned” from 180° (superhydrophobic) to 0° (superhydrophilic). Similarly, using the values of $(\rho_S A_{SL})$, one can calculate the contact angle of water on a sheet of monolayer graphene supported by the solid substrate, denoted as θ_{GS} , by using only a single undetermined parameter, δ_{SG} . Figure 3(a) shows the calculated θ_{GS} as a function of θ_S for three arbitrary values of δ_{SG} (5, 4, and 3 \AA). The line of $\theta_{GS} = \theta_S$, which corresponds to the wetting transparency of monolayer graphene, is also shown for reference. For each δ_{SG} value considered, there is a significant deviation from the wetting transparency, suggesting that graphene is only partially

transparent to wetting. Note that our model does not consider the effect of electrostatic interactions or of the formation of hydrogen bonds between liquid and the charge impurities on the solid surface, which is expected to be less sensitive to the value of δ_{SG} [15]. Experimentally, considering different values of δ_{SG} introduced spatially during the transfer process of CVD graphene onto different substrates [33], there is a higher likelihood to observe some wetting transparency for $40^\circ < \theta_S < 90^\circ$ (note that this is within the θ_S range studied in Ref. [11]). However, as shown in Fig. 3(a), since the intermolecular distance is typically greater than 3 \AA [15], we predict that the deviation from the wetting transparency should be more significant when $\theta_S < 40^\circ$. Along with our previous analysis, we also predict that (i) $\theta_{GS} > \theta_S$ when $\theta_S < 40^\circ$ and (ii) $\theta_{GS} < \theta_S$ when $\theta_S > 90^\circ$. Note that here we assume that the vdW interaction potential dominates the interactions between liquid and solid. In other words, the wetting transparency of monolayer graphene will break down significantly on superhydrophobic and most superhydrophilic substrates.

In order to further test the theory, we carried out static contact angle measurements of water on CVD-grown graphene supported by the following substrates: (i) as-received 300 nm thick SiO_2 on a Si wafer (AR- SiO_2), (ii) oxygen plasma-cleaned 300 nm thick SiO_2 on a Si wafer (OP- SiO_2), (iii) self-assembled monolayer of octadecyltrichlorosilane (OTS) on 300 nm SiO_2 (OTS- SiO_2), and (iv) silica nanoparticles on glass (silica NP) [34]. The experimental methods of CVD graphene synthesis and transfer are described elsewhere [35,36]. The measured values of θ_S and θ_{GS} are shown in Figs. 3(a) and 3(b). For water on hydrophobic substrates (OTS- SiO_2 and silica NP), the measured θ_{GS} values never exceed 95° , which confirms the theoretically predicted 96° contact angle. In addition, as predicted, $\theta_{GS} > \theta_S$ is clearly observed on superhydrophilic substrates (OP- SiO_2). Although we did observe some degree of wetting transparency ($|\theta_S - \theta_{GS}| < 10^\circ$) in the three samples corresponding to $30^\circ < \theta_S < 90^\circ$ [see Fig. 3(a)], according to our theoretical analysis, these values occur in the range where our calculated curves fall near the perfect wetting transparency line. The measured contact angles in other samples [$\theta_S < 30^\circ$ or $\theta_S > 90^\circ$; see Fig. 3(b)] confirm that the deviation of θ_{GS} from θ_S becomes much more significant on superhydrophobic and superhydrophilic substrates. It is also noteworthy that, since adding more graphitic layers further screens the effect of the underlying substrate, the cases for multilayer graphene ($N \geq 2$) simply decrease the wetting transparency.

In summary, by combining theoretical analysis, MD simulations, and contact angle measurements, we have shown that graphene is not entirely transparent to wetting. Although the wetting behavior of the substrate does get partially transmitted through a sheet of monolayer

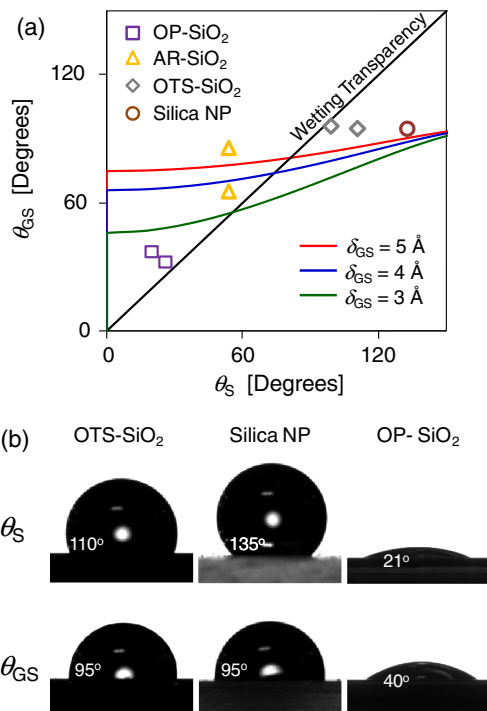


FIG. 3 (color online). (a) Calculated θ_{GS} as a function of θ_S for the three values of δ_{SG} considered (color curves) and experimentally measured values of θ_{GS} and θ_S on various substrates (color symbols). The line of $\theta_{GS} = \theta_S$ (black line), which corresponds to the wetting transparency, is shown as a reference. (b) Photographs of water drops and measured values of θ_S and θ_{GS} on an OTS- SiO_2 , silica NP, or OP- SiO_2 substrate with and without a sheet of monolayer graphene between them.

graphene, the wetting transparency breaks down significantly on superhydrophobic and superhydrophilic substrates. We believe that the manipulation of wetting properties on graphene-coated surfaces will be greatly facilitated by the fundamental principles and theoretical analysis presented here.

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- [1] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov, *Science* **306**, 666 (2004).
- [2] A. K. Geim and K. S. Novoselov, *Nature Mater.* **6**, 183 (2007).
- [3] A. M. Affoune, B. L. V. Prasad, H. Sato, T. Enoki, Y. Kaburagi, and Y. Hishiyama, *Chem. Phys. Lett.* **348**, 17 (2001).
- [4] A. K. Manna and S. K. Pati, *Chem. Asian J.* **4**, 855 (2009).
- [5] A. Ghosh, K. S. Subrahmanyam, K. S. Krishna, S. Datta, A. Govindaraj, S. K. Pati, and C. N. R. Rao, *J. Phys. Chem. C* **112**, 15 704 (2008).
- [6] C. Gomez-Navarro, J. C. Meyer, R. S. Sundaram, A. Chuvilin, S. Kurasch, M. Burghard, K. Kern, and U. Kaiser, *Nano Lett.* **10**, 1144 (2010).
- [7] S. Bae *et al.*, *Nature Nanotech.* **5**, 574 (2010).
- [8] J. Rafiee, M. A. Rafiee, Z.-Z. Yu, and N. Koratkar, *Adv. Mater.* **22**, 2151 (2010).
- [9] S. R. Wang, Y. Zhang, N. Abidi, and L. Cabrales, *Langmuir* **25**, 11 078 (2009).
- [10] H. Zhou *et al.*, *Phys. Rev. B* **85**, 035406 (2012).
- [11] J. Rafiee, X. Mi, H. Gullapalli, A. V. Thomas, F. Yavari, Y. Shi, P. M. Ajayan, and N. A. Koratkar, *Nature Mater.* **11**, 217 (2012).
- [12] A. Tuteja, W. Choi, J. M. Mabry, G. H. McKinley, and R. E. Cohen, *Proc. Natl. Acad. Sci. U.S.A.* **105**, 18 200 (2008).
- [13] A. W. Adamson and A. P. Gast, *Physical Chemistry of Surfaces* (Wiley, New York, 1997).
- [14] T. Ingebrigtsen and S. Toxvaerd, *J. Phys. Chem. C* **111**, 8518 (2007).
- [15] J. N. Israelachvili, *Intermolecular and Surface Forces* (Academic, Burlington, MA, 2011).
- [16] L. A. Girifalco, M. Hodak, and R. S. Lee, *Phys. Rev. B* **62**, 13 104 (2000).
- [17] D. D. L. Chung, *J. Mater. Sci.* **37**, 1475 (2002).
- [18] D. B. Hough and L. R. White, *Adv. Colloid Interface Sci.* **14**, 3 (1980).
- [19] C. J. Drummond and D. Y. C. Chan, *Langmuir* **13**, 3890 (1997).
- [20] C. J. Shih, S. Lin, M. S. Strano, and D. Blankschtein, *J. Am. Chem. Soc.* **132**, 14 638 (2010).
- [21] D. Van der Spoel, E. Lindahl, B. Hess, G. Groenhof, A. E. Mark, and H. J. C. Berendsen, *J. Comput. Chem.* **26**, 1701 (2005).
- [22] N. R. Tummala and A. Striolo, *J. Phys. Chem. B* **112**, 1987 (2008).
- [23] H. J. C. Berendsen, J. R. Grigera, and T. P. Straatsma, *J. Phys. Chem.* **91**, 6269 (1987).
- [24] S. Miyamoto and P. A. Kollman, *J. Comput. Chem.* **13**, 952 (1992).
- [25] T. Darden, D. York, and L. Pedersen, *J. Chem. Phys.* **98**, 10 089 (1993).
- [26] L. Verlet, *Phys. Rev.* **159**, 98 (1967).
- [27] G. Bussi, D. Donadio, and M. Parrinello, *J. Chem. Phys.* **126**, 014101 (2007).
- [28] G. Saville, *J. Chem. Soc., Faraday Trans. 2* **73**, 1122 (1977).
- [29] A. Checco, P. Guenoun, and J. Daillant, *Phys. Rev. Lett.* **91**, 186101 (2003).
- [30] T. Werder, J. H. Walther, R. L. Jaffe, T. Halicioglu, and P. Koumoutsakos, *J. Phys. Chem. B* **107**, 1345 (2003).
- [31] T. Pompe and S. Herminghaus, *Phys. Rev. Lett.* **85**, 1930 (2000).
- [32] L. Boruvka and A. W. Neumann, *J. Chem. Phys.* **66**, 5464 (1977).
- [33] A. Reina, X. Jia, J. Ho, D. Nezich, H. Son, V. Bulovic, M. S. Dresselhaus, and J. Kong, *Nano Lett.* **9**, 3087 (2009).
- [34] J. Bravo, L. Zhai, Z. Wu, R. E. Cohen, and M. F. Rubner, *Langmuir* **23**, 7293 (2007).
- [35] Q. H. Wang *et al.*, *Nat. Chem.* **4**, 724 (2012).
- [36] N. Petrone, C. R. Dean, I. Meric, A. M. van der Zande, P. Y. Huang, L. Wang, D. Muller, K. L. Shepard, and J. Hone, *Nano Lett.* **12**, 2751 (2012).