Comment on "Dynamic Catalyst Restructuring during Carbon Nanotube Growth"

■ In a recent study, Moseler et al.[1] use environmental transmission electron microscopy to observe the restructuring of solid Ni catalyst during the growth of carbon nanotubes. They also simulate the evolution of the catalyst shape during growth using molecular dynamics and derive a continuum model to describe this process. The continuum model, which assumes that the catalyst restructuring is capillary-driven and surface-diffusion-mediated, is found to give quantitative agreement with the experimentally measured time scales. However, in this letter, we would like to correct the assertion by Moseler et al. that ref 2 and ref 3 (ref 32 and ref 33 in the article) contain experimental evidence that supports this continuum model. This is not the case. Rather, these works contain derivations of continuum models that are mathematically equivalent to that derived by Moseler et al. Experimental evidence which supports such models is available elsewhere (e.g., ref 4).

In fact, the theory of capillary penetration was extended to droplets of finite size by Marmur,[2] whose model we generalized and tested in the context of carbon nanotubes and metal nanoparticles via molecular dynamics simulations.[3,5,6] The sole distinction between the model of Moseler et al. and that in refs 2, 3, 5, and 6 lies in the mass-transport mechanism: refs 2, 3, 5, and 6 consider a fully developed Newtonian fluid flow, while Moseler et al. model a steady surface diffusion current. For constant transport coefficients (i.e., spatially independent fluid viscosity μ and surface diffusion coefficient D_s), the resultant equations of motion for the tail length (eq 2 in ref 1 and eq 2 in ref 5) have exactly the same form. An analytic solution to this particular ordinary differential equation is known,[5] and as we will show below, it is easily generalized to deal with diffusion coefficients $D_s(z)$ that vary in a piece-wise manner along the tube axis z (as is the case in eqs 3 and 4 of ref 1).

Following ref 5, we first use volume conservation to eliminate the tail length $L(t)$ from eq 3 of ref 1 and then integrate the resultant differential equation for the outer head radius $R(t)$. This yields

$$\frac{t - t_0}{t_s} = -\int_{R(t_0)/r}^{R(t)/r} \frac{\tilde{R}^3(\tilde{R}_f^3 - \tilde{R}^3 - \alpha)}{1 + \tilde{R}\cos\theta}\, d\tilde{R} \qquad (1)$$

where $t_s = 4r^4 k_B T/(3\gamma\Omega^2\rho_s D_s^{tube})$ and $\tilde{R}_f = R_f/r$; $\theta, r, R_f, k_B, T, \gamma, \Omega, \rho_s$, and D_s^{tube} bear the same meaning as in ref 1, and α is a dimensionless constant whose value depends on the particular approximation to the catalyst volume and the piece-wise linear function $D_s(z)$. In the context of eq 3 of ref 1, $\alpha = 3L_{exit}(1 - D_s^{tube}/D_s^{exit})/(4r) + 1/2$, whereas the approximation given in eq 4 of ref 1 would lead to $\alpha = 3[L_{kink}(1 - D_s^{tube}/D_s^{kink}) + L_{step}(1 - D_s^{tube}/D_s^{step}) + L_{hi}(1 - D_s^{tube}/D_s^{hi})]/(4r) + 1/2$. Note that the 1/2 in both expressions for α comes from an overestimate of the catalyst volume in the approximation used in ref 1. References 2, 3, 5, and 6 make use of a more accurate approximation for the catalyst volume, differing from that above by a 1/2; that is, $\alpha = 3L_{exit}(1 - D_s^{tube}/D_s^{exit})/(4r)$. Regardless of the approximation to α used, the evaluation of the integral in eq 1 is analogous to that in ref 5.

Finally, we wish to comment on the authors' assertion that, in experiment and in their MD model, "the equilibrium contact angle of Ni on graphene, θ, is $\sim$180°, indicating that the particle does not wet the CNT". The contact angle strongly affects the capillary forces that drive catalyst withdrawal and restructuring, but Moseler et al. do not describe exactly how they define and measure the equilibrium value $\theta \approx 180°$ in their dynamic simulation and experiments. There is also no quantitative data for θ in the experimental works they cite. Prior studies have shown that the contact angle of Ni[7] (and Fe[8]) on graphite can range from $\sim$50 to $\sim$120°, depending on the absorbed carbon concentration, which suggests that absorbed carbon may also play an important role in determining the dynamics of catalyst restructuring during carbon nanotube growth.

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LETTER TO THE EDITOR