

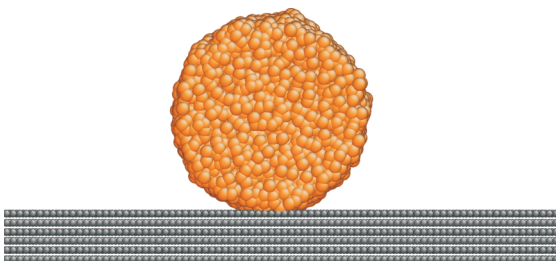
## Reply to “Comment on ‘Dynamic Catalyst Restructuring during Carbon Nanotube Growth’”

■ In their comment, Schebarchov and Hendy point out that we cited<sup>1</sup> their previous work,<sup>2</sup> as well as Marmur's seminal work,<sup>3</sup> not only as theoretical papers but also with the adjective “experimental”, while Schebarchov and Hendy<sup>2</sup> and Marmur<sup>3</sup> were theoretical papers, with no experiments, unlike our work,<sup>3</sup> where extensive theoretical calculations are supported by state of the art experiments.

Since Schebarchov and Hendy<sup>2</sup> contained not only theoretical calculations but also an excellent review of the most relevant experimental works, we assumed we could use it to direct the reader who wanted to have a good list of experimental works, not just two relevant previous theoretical references. Indeed Schebarchov and Hendy<sup>2</sup> state that “there is certainly experimental evidence that nanoparticles can be drawn easily into open CNTs. For instance, nanoparticles of various transition metals such as Pd, Ni, and Cu, which are used as catalysts during the growth of CNTs *via* chemical vapor deposition (CVD) techniques,<sup>5</sup> are often found encapsulated in CNTs during and after the CVD process.<sup>6–8</sup> In addition, Hayashi *et al.* have recently synthesized vertically aligned CNTs filled with segmented Pd–Co nanocomposites,<sup>9</sup> and Zhang *et al.* report the filling of CNTs by nonwetting Cu nanodroplets.<sup>10</sup> These experimental observations suggest that capillary forces may be sufficient to drive filling of CNTs by metallic nanoparticles despite the failure of these metals to wet graphite.” It was precisely this experimental evidence we wanted to highlight when citing Schebarchov and Hendy.<sup>2</sup> We thus stand by our citation of Schebarchov and Hendy's paper, even against the request of Schebarchov and Hendy to not cite their paper in relation to any experiment.

Schebarchov and Hendy then suggest that, instead of their very relevant previous paper,<sup>2</sup> we should have cited Willmott *et al.*<sup>11</sup> We see no reason for us to cite Willmott *et al.* because it reports experiments on a system that is irrelevant to our work: water in contact with polytetrafluoroethane microcapillaries,<sup>11</sup> whereas, as discussed above, Schebarchov and Hendy<sup>2</sup> provide a good overview of experiments directly relevant for our paper. As evident by reading the title of our paper,<sup>1</sup> we deal with nanotubes' growth and not with water in contact with polytetrafluoroethane microcapillaries. We can only assume this point was missed by Schebarchov and Hendy when writing their comment.

Schebarchov and Hendy go on to comment that their previous paper,<sup>2</sup> as well as Marmur,<sup>3</sup> contains derivations of continuum models mathematically equivalent to ours.<sup>1</sup> Unfortunately, we cannot agree with this statement either. The model of Marmur<sup>3</sup> as well as the extensions of Schebarchov and Hendy<sup>2,12</sup> differ from our model<sup>1</sup> in the mass transport mechanism. We showed by our molecular dynamics (MD) simulations<sup>1</sup> that catalyst particles under typical CNT growth



**Figure 1.** Snapshot of a Langevin molecular dynamics simulation of a Ni<sub>12000</sub> droplet at 2000 K on a graphite surface for the same MD model as in ref 1.

conditions are still solid and deform *via* surface diffusion, while Marmur treats liquid droplets.<sup>3</sup> Schebarchov and Hendy apply Marmur's model to CNTs,<sup>2,12</sup> taking for granted that transition metal particles are liquid during CNT growth by claiming that the experimental “capillary adsorption of nonwetting Cu nanodroplets by carbon nanotubes”<sup>2</sup> can be explained in this way. It appears that Schebarchov and Hendy failed to notice that Zhang *et al.*<sup>10</sup> report experiments 185 K below the copper melting point, which makes their assumption of a “fully Newtonian fluid flow” unlikely.<sup>13</sup> We certainly consider it interesting that Marmur's model and our model lead to a similar final equation, despite the different physical processes governing the dynamics of Marmur's liquid droplets and our solid particles. This similarity can be traced back to the fact that, in both cases, the transport velocity is proportional to the driving capillary pressure difference. Note, however, that the prefactors of this proportionality are different leading to completely different time scales of the catalyst dynamics.

Schebarchov and Hendy conclude their comment by discussing the equilibrium contact angle  $\theta \sim 180^\circ$  used in our model. We estimated this  $\theta$  from our MD model using the sessile drop method.<sup>16</sup> Within this model, a Ni<sub>12000</sub> droplet at 2000 K does not wet graphite (see Figure 1). Of course, experimentally,  $\theta$  might be much smaller since defects increase the adsorption energy between graphite and Ni, an effect that has been discussed in full length in our article.<sup>1</sup> Similarly, adsorbed C adatoms could decrease  $\theta$ . Nevertheless, the experiments cited by us<sup>17–19</sup> show evidence for a fast dewetting process and support a contact angle that should be close to  $180^\circ$  on an ideal graphite surface.

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