The existence and properties of gases adsorbed within interstitial channels of nanotube bundles

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Abstract

We analyze the relationship between our group’s results and those of three recent papers about gases in interstitial channels within nanotube bundles. In particular, we explain the relation between our prediction about bundle dilation upon interstitial adsorption (questioned in some way in these works) and their results.
During the decade since their first observation, carbon nanotubes have provided a stimulus for extensive research, leading to many exciting discoveries as well as a number of controversies. Recently, three studies have explored different aspects of our group’s work concerning gas adsorption within and outside of nanotube bundles. Each of these papers draws conclusions that are, in some sense, critical of our group’s results. This Brief Report describes these studies very briefly and explains the relation between our work and those studies. The fact that these papers all appeared quite recently shows the importance of the subject. Evidently, a mutual “discussion” of these controversial questions is warranted.

We believe that experimental data is necessary to resolve some of these questions, but others can be answered without recourse to experiments.

All three papers deal with the phases of adsorbed gases in interstitial channels (ICs) within nanotube bundles. Numerous theoretical studies have explored these phases for He, H\textsubscript{2} and Ne which are small enough to fit comfortably within the ICs. While several reports concerning possible experimental observation of IC adsorption have appeared, other articles have expressed contrary opinions about their existence. This difference may well be a consequence of different kinds of experimental samples.

The three papers discussed here are related, in one way or another, to the question of “dilation” of the nanotube bundle. The idea of dilation is simply that a bundle of tubes will dilate, due to adsorption, in order to accommodate the adsorbate. We evaluated the effect of dilation for the case of H\textsubscript{2} in ICs and concluded that it can have a dramatic effect on the ground state energy of the H\textsubscript{2} fluid.

One of the papers discussed here is by Gordillo, Boronat and Casulleras (GBC). This paper reports extensive, state-of-the-art investigations of dilation of bundles containing H\textsubscript{2} at temperature \(T = 0\). As these authors note, their results agree with ours for the case in which they assume the same form of the C-H\textsubscript{2} pair interaction and the same force constant of the inter-tube interaction. One of the main points made by GBC, however, is that the parameters of the C-H\textsubscript{2} interaction might well differ from what was assumed in our work. In that case, they find quite different results. What GBC omitted to mention is that we noted exactly the same point in our original paper, from which we quote: “One factor to bear in mind is the sensitivity of these results to the potential parameters. As examples, in the case of both H\textsubscript{2} and CH\textsubscript{4}, a 2.5% decrease in the gas-carbon length parameter... results in about a 25% increase in the magnitude of [the chemical potential]”. In our second
paper on the subject, we presented a graph showing this dependence on the value of this uncertain parameter. The fact is that all such theoretical studies rely on inadequately known interactions; the dilation phenomenon is one for which the experiment is a exquisitely sensitive probe of these interactions. Thus, there is no conceptual or theoretical controversy but there does exist an open question that can be addressed in future experimental studies. We note, in addition, that both our work and GBC employ a simplified model in which the nanotube-molecule interaction neglects the corrugation of the potential. While this neglect is usually well-justified in the case of adsorption on planar graphite (for which the band structure correction to the effective mass is small), one study of He in the IC yielded a huge mass correction ($m_{\text{band}} / m_{\text{bare}}$ as high as a factor 20); such a large corrugation drastically changes the energetics of adsorption. Incorporating this effect requires knowledge of the chirality of the tubes forming each IC, which is not known in the case of current experiments. Until we have resolved these open questions, quantitative predictions are uncertain.

There is one further point made in the GBC paper upon which we comment. These authors affirm that “Probably, even if such effect [dilation] is indeed present, its manifestation could be hardly observed due to the present experimental uncertainties.” We respectfully disagree, because neutron or X-ray diffraction is capable of measuring the predicted dilation, an example of which is discussed below. In analyzing such an experiment, it is necessary to take into account the effect of a polydisperse distribution of nanotube sizes. In addition, finite bundle size effects necessitate more careful modeling of the dilation problem than has been done thus far.

The second paper upon which we comment is by Brualla and Gordillo (BG). These authors compute the gas-liquid critical temperature ($T_c$) of an anisotropic fluid consisting of Ne atoms in ICs that experience interchannel interactions. In their paper BG describe our paper’s results as follows: “There is even an estimation of a gas-liquid transition critical temperature in the case of Ne, using a 3D modified anisotropic Ising model to get $T_c$. A comparison between the number obtained in that approximation ($T_c = 63.8 \text{ K}$) and the one in the present work [12 K] shows that in the neon case that Ising model is completely inadequate, at least with the parameters given in that reference.”

This description of and comparison with our calculations is misleading in two important respects. One is that our calculations take into account the predicted dilation; their calculations ignore this effect. The key significance of the predicted dilation is that it greatly
increases the binding of the Ne fluid so that $T_c$ is much higher than is found without taking
dilation into account. Hence, it is not appropriate to compare the two sets of results for $T_c$. The second issue pertains to our use of the Ising model, referred to above as “seriously inadequate”, because of the alleged disagreement in $T_c$. In a set of papers, we have found that this Ising model gives semiquantitative agreement with a more realistic continuum method, perturbation theory (which is well justified in the case of weak interactions between molecules in neighboring ICs). In summary, the factor of five disagreement between our $T_c$ values of those of BG are attributable to the important role of dilation within our theory (absent from theirs). If the dilation were omitted from our theory (or absent in the real system), the value of $T_c$ predicted by our theory, with the Ising model, would be 11.4 K for the (5,5) nanotube bundle case, nearly coincident with the simulation value (12 K) found by BG.

We turn next to recent experimental results of Bienfait et al. These authors concluded from their data between 77 K and 96 K that Ar atoms in ICs do not lead to dilation of the bundles. Although this finding was interpreted as disagreeing with our predictions, this is not actually the case. Our prediction was that Ar within ICs would have a chemical potential $\mu_{IC} = -1270$ K at $T = 0$. This value is much lower than the value of $\mu$ calculated in the absence of dilation, indicating that dilation would occur (at $T = 0$) if the atoms are located within ICs. However, there is no reason to expect such preferential IC adsorption because, for Ar atoms, the groove region of the external surface of the bundle is energetically more attractive. The same potential energy model used in the IC predicts a single atom binding energy to be $E_{external} = -1550$ K. At low $T$, however, the groove atoms form a condensed state with much higher binding energy and chemical potential. Taking into account just nearest neighbor interactions within the groove yields an estimate $\mu_{external} = -1650$ K. This groove phase is the lowest free energy (and chemical potential) state predicted for the case of Ar interacting with nanotubes. At higher pressure and chemical potential, of course, less strongly bound phases are expected to form; we have carried out simulation studies of these on the external surface. The so-called three-stripe phase was found to appear at $\mu_{3stripe} = -1270$ K, while the external surface’s monolayer forms at $\mu_{mono} = -1040$ K (at $T = 30$ K). Thus, the IC adsorption and accompanying dilation is predicted to be energetically comparable with the three-stripe phase at very low $T$ but we do not have any prediction for the dilation’s behavior at higher $T$. Our intuition suggests that the
confinement within the ICs is inherently a low entropy situation (because of relatively high excitation energy). Hence a phase (like the monolayer) which is somewhat less favored energetically than the dilated IC may well become more favored at finite $T$. However, we reiterate that our calculations comparing the energies of these phases are sensitive to uncertain assumptions, which require testing by such experiments as these.

In our opinion, the strongest evidence for the existence of IC adsorption comes from the large isotope effect in the isosteric heat reported by Tate et al\textsuperscript{12} for $\text{H}_2$ and $\text{D}_2$ at the lowest coverages. Our modeling of these problems has yielded a difference in isosteric heats for the ICs that is somewhat smaller than that found experimentally: 140 K when dilation is included vs. about 200 K found in the experiments. For the grooves, in contrast, our model yields a value near 50 K that is completely incompatible with the experimental data. While the individual results for the isosteric heats of $\text{H}_2$ and $\text{D}_2$ are sensitive to the model potential used, the isotope energy \textit{shift} tends to be particularly sensitive to the geometry of the confining space (as expected for zero-point energy).

We summarize the situation as follows. All theoretical studies of nanotube adsorption have made numerous simplifying assumptions about the geometry and interactions. Small differences between different models can yield quite different results because of the sensitivity of the energy within the IC environment. On the theoretical side, there is no doubt that dilation occurs for an IC phase at low $T$ (except with a unique choice of interaction length), but careful studies at finite $T$ and finite pressure are needed in order to make comparison with experiments. Finally, we note that the theoretical calculations described here rely on the assumption of perfect, identical and parallel nanotubes. This idealization must be sacrificed in order to make quantitative comparison with experiments, especially in those situations where energy differences are small or where the phenomena are particularly sensitive to the assumptions\textsuperscript{24}.

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1. M. Bienfait, P. Zeppenfeld, N. Dupont-Pavlovsy, J.P. Palmari, M.R. Johnson, T. Wilson, M. DePies, O.E. Vilches, Phys. Rev. Lett. 91, 035503 (2003).
2. M. C. Gordillo, J. Boronat and J. Casulleras, Phys. Rev. B 68, 125421 (2003).
3. L. Brualla and M.C. Gordillo, Phys. Rev. B 68, 075423 (2003).
4. M. Mercedes Calbi, Flavio Toigo and Milton W. Cole, Phys. Rev. Lett. 86, 5062 (2001).
5. M. M. Calbi, F. Toigo and M. W. Cole, J. Low Temp. Phys. 126, 179 (2002).
6. M. Mercedes Calbi, Silvina M. Gatica, Mary J. Bojan, George Stan and Milton W. Cole, Rev. Mod. Phys. 73, 857 (2001).
7. G. Stan, M.J. Bojan, S. Curtarlo, S.M. Gatica, and M.W. Cole, Phys. Rev. B 62, 2173 (2000).
8. Q.Y. Wang, S.R. Challa, D.S. Sholl, and J.K. Johnson, Phys. Rev. Lett. 82, 956 (1999).
9. Q.Y. Wang and J.K. Johnson, J. Phys. Chem. B 103, 4809 (1999).
10. J. Boronat, M.C. Gordillo, J. Casulleras, J. Low Temp. Phys. 126, 199 (2002).
11. Y. Ye, C.C. Ahn, C. Witham, B. Fultz, S. Liu, A.G. Rinzler, D. Colbert, K.A. Smith, and R.E. Smalley, Appl. Phys. Lett. 74, 2307 (1999).
12. T. Wilson, A. Tyburski, M.R. DePies, O.E. Vilches, B. Becquet, and M. Bienfait, J. Low Temp. Phys. 126, 403 (2002); M. Muris, M. Bienfait, P. Zeppenfeld, N. Dupont-Pavlovsy, M. Johnson, O.E. Vilches, and T. Wilson, Appl. Phys. A: Mater. Sci. Process. A74, S1293 (2002).
13. W. Teizer, R.B. Hallock, E. Dujardin, and T.W. Ebbesen, Phys. Rev. Lett. 82, 5305 (1999) and 84, 1844 (2000).
14. S. Talapatra, A.Z. Zambano, S.E. Weber, and A.D. Migone, Phys. Rev. Lett. 85, 138 (2000).
15. A.D. Migone and S. Talapatra, in the Encyclopedia of Nanoscience and Nanotechnology, edited by H. S. Nalwa, American Scientific Publishers, in press, 2004.
16. A. Mizel, L.X. Benedit, M.L. Cohen, S. Louie, A. Zettl, N.K. Budraa, and W.P. Beyermann, Phys. Rev. B 60, 3264 (1999).
17. J. Tang, L. Qin, T. Sasaki, M. Yuclasaka, A. Matsushita, and S. Ijima, Phys. Rev. Lett. 85, 1887 (2000).
18. L.W. Bruch, in Phase transitions in surface films 2, ed. H. Taub, G. Torzo, H. J. Lauter, and S. C. Fain, Jr., Plenum, New York, pp.67-82 (1991).
19 M. Boninsegni, S. Lee, V.H. Crespi, Phys. Rev. Lett. 86, 3360 (2001).
20 S. Amelinckx, A. Lucas, and P. Lambin, Rep. Prog. Phys. 62, 1471 (1999).
21 M. W. Cole, V. H. Crespi, G. Stan, J. M. Hartman, S. Moroni, C. Ebner and M. Boninsegni, Phys. Rev. Lett. 84, 3883 (2001).
22 S. M. Gatica, M. M. Calbi and M. W. Cole, J. Low Temp. Phys. 133, 399 (2003).
23 S.M. Gatica, M.J. Bojan, G. Stan, and M.W. Cole, J. Chem. Phys. 114, 3765 (2001).
24 W. Shi and J. K. Johnson, Phys. Rev. Lett. 91, 015504 (2003).