

# A comment on the order of the wetting transition at a solid–fluid interface

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also significantly smaller ( $1.09 \pm 0.04$  Hz) than the corresponding value in  $\text{BH}_4^-$ , 81.00 Hz.<sup>8</sup> The data in Table I also indicate that the primary isotope effect on  $^1J(\text{N,H})$  is very small, less than 0.2 Hz. A summary of isotope effects on spin-spin coupling constants has recently been given by Everett.<sup>9</sup> Although it is possible to rationalize primary isotope effects on coupling constants, the interpretation of secondary isotope effects is more difficult.

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## COMMENTS

### A comment on the order of the wetting transition at a solid-fluid interface

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It is the purpose of this Comment to bring to attention some important discrepancies between the results obtained in two recent theoretical investigations of the order of the wetting transition at a solid-gas interface. Teletzke *et al.*<sup>1</sup> and the present authors<sup>2</sup> reported the results of independent analyses of this transition for certain models of solid-fluid interfaces. Both groups employed a mean-field free energy functional of the type introduced earlier by Sullivan<sup>3</sup> and modeled the solid-fluid interactions by an external potential  $u_e(x)$ . Depending on the choice of potential functions, they found that the transition from partial to complete wetting, which occurs at a temperature  $T_{cw}$  below the bulk fluid critical temperature, could be a first-order surface phase transition, as predicted by Cahn<sup>4</sup> and calculated by Ebner and Saam,<sup>5</sup> or a second-order transition as found by Sullivan<sup>3</sup> in his analysis of a special case of the free energy functional. The two groups agree that the order of the transition depends on the relative strengths and ranges of the attractive part of the solid-fluid and fluid-fluid potentials but they disagree on several specific details. In particular, when  $u_e(x)$  was taken to be a Lennard-Jones 9-3 substrate potential and the attractive forces between fluid molecules were modeled by a Lennard-Jones 12-6 potential, our calculations<sup>2,6</sup> showed that the transition was always first order. This conclusion was supported by an approximate analysis<sup>2</sup> of the dependence of the interfacial free energy on the coverage which suggested that an infinitely thick wetting film should always be a metastable state of the system for  $T < T_{cw}$  and, hence, the transition should always be first order for such a

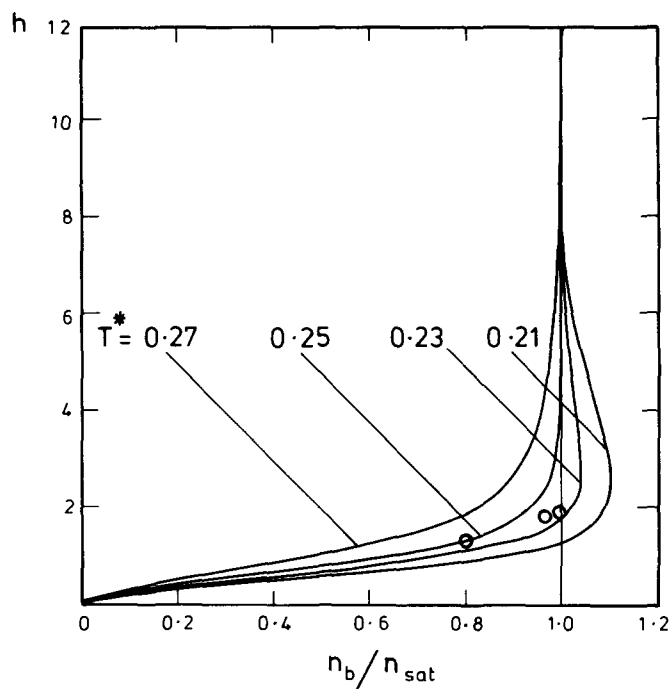


FIG. 1. Adsorption isotherms calculated for a 9-3 substrate potential with  $W_{9,3} = 7.0$  and  $d = 1.0$ . The solid curves are the results of Ref. 1 (Fig. 3) at four reduced temperatures  $T^*$ . The circles are our present results at  $T^* = 0.21$ . Note that the point at saturation ( $n_b/n_{sat} = 1$ ) corresponds to a metastable film.  $n_b$  is the density of the bulk gas.  $h$  is the film thickness in reduced units. The solid curves are consistent with a second-order transition at  $T_{cw}^* = 0.24$  while the present results indicate a first-order transition slightly below 0.21.

model system. Teletzke *et al.*,<sup>1</sup> however, found from their calculations for a Lennard-Jones 9-3 substrate that the transition was not always first order but was second-order for certain choices of potential parameters. Given that the order of the wetting transition is not yet determined experimentally<sup>1-3</sup> and that the Lennard-Jones 9-3 substrate is quite a realistic and commonly used model, we believe it is important to attempt to establish with more certainty what is expected theoretically.

With this aim we repeated the calculations of Ref. 1 using the same "van der Waals integral theory," with identical potentials and parameters, as those authors. We consider first the results for the two cases in which solid-fluid and fluid-fluid potentials are modeled by exponential functions. For the first of these<sup>1</sup> ( $W_{\text{exp}} = 0.7$  and  $d = 0.9$ ) we calculate a second-order transition in agreement with Ref. 1. We find  $T_{cw}^*$ , the reduced transition temperature, is 0.251 which is quite close to their value 0.24. Teletzke *et al.* plot adsorption isotherms, and our results, for temperatures  $T^* = 0.25$  and 0.23, lie very close to theirs (Fig. 1 of Ref. 1) for bulk densities  $\leq$  the saturated gas density. In the second exponential model ( $W_{\text{exp}} = 0.5$  and  $d = 2.0$ ), we find that the transition is first order, in agreement with Ref. 1, but occurs at  $T_{cw}^* \leq 0.05$  rather than  $T_{cw}^* = 0.11$ , as given in Ref. 1. Moreover our results for the adsorption isotherms differ substantially from those plotted in Fig. 2 of Ref. 1. For example, at  $T^* = 0.13$  and  $n_b/n_{\text{sat}} = 0.9$  we find a (metastable) thin film and a (stable) thick film and calculate the thickness of the latter to be  $h \sim 7.4$  while Teletzke *et al.* obtain  $h \sim 5.6$ .

Turning now to the results for the Lennard-Jones 9-3 solid-fluid potential we find more serious discrepancies. With parameters  $W_{9,3} = 7.0$  and  $d = 1.0$ , Teletzke *et al.* calculated a second-order wetting transition at  $T_{cw}^* = 0.24$  whereas we find a first-order transition at a temperature just below 0.21. In Fig. 1 we plot our results for the adsorption isotherm at  $T^* = 0.21$  and compare with the isotherms of Ref. 1. We find that the film thickness remains finite ( $h \sim 2.0$ )

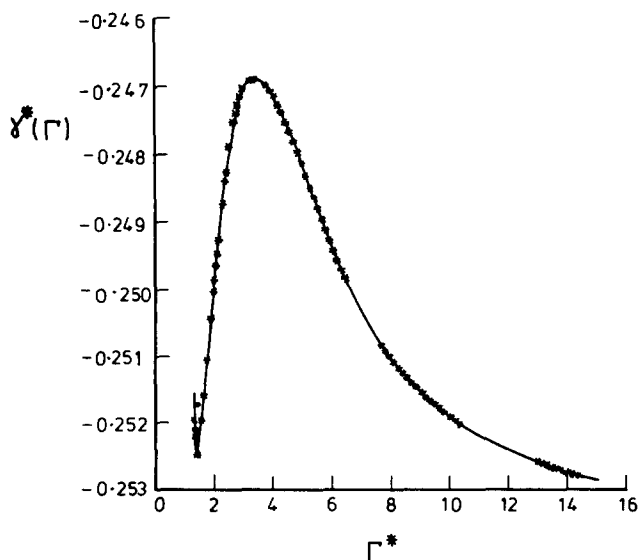


FIG. 2. The excess surface grand potential  $\gamma^*(\Gamma)$  (in reduced units) at saturation as a function of the reduced coverage  $\Gamma^*$  for the model described in Fig. 1 at  $T^* = 0.21$ .

at saturation as is appropriate to a thin film. At the wetting transition this film coexists with the infinitely thick film while for the slightly higher temperature the thin film is slightly metastable.<sup>2</sup> By contrast, Teletzke *et al.*<sup>1</sup> find isotherms characteristic of a continuous, second-order transition. In order to demonstrate more explicitly the first-order character of our calculated transition we plot in Fig. 2 the surface excess grand potential per unit area  $\gamma(\Gamma)$  as a function of the coverage  $\Gamma$  for  $T^* = 0.21$  and  $n_b/n_{\text{sat}} = 1$ . This function<sup>7</sup> has a minimum at a small value of reduced coverage  $\Gamma^* = \Gamma l^2 \sim 1.4$  corresponding to the thin film with  $h \sim 2.0$ . This film is metastable since the value of  $\gamma^* \equiv bl^2 \gamma/a$  at the minimum ( $-0.2525$ ) is higher than the value corresponding to the minimum for infinite coverage which is  $\gamma^*(\infty) \equiv \gamma_{sl}^* + \gamma_{lg}^* = -0.254$ . Here  $\gamma_{sl}$  and  $\gamma_{lg}$  are the solid-liquid and liquid-gas surface tensions, respectively. The minima are separated by a pronounced maximum giving a metastability barrier<sup>2</sup> of height 0.0072. At the wetting transition  $\gamma(\Gamma)$  is close to that shown in Fig. 2 but the values of the function at the minima are equal indicating coexistence of the two films. Such behavior signals unambiguously a first-order phase transition.<sup>2</sup> Note, moreover, that since metastability barrier remains substantial at the wetting transition, the latter cannot be regarded as "weakly" first order in this case. We calculated the thick-thin film transition line, along which thick and thin film co-exist above  $T_{cw}$ , and found it terminated at a surface critical temperature  $T_{cs} \simeq 0.24$ . Since their transition is second order, Teletzke *et al.* do not obtain such a line.

The second 9-3 model sets  $W_{9,3} = 12.0$  and  $d = 1.0$ . For this case we agree with Teletzke *et al.* that the transition is first order but we calculate a much lower transition temperature  $T_{cw}^* \leq 0.08$  than their value of 0.14. Our results for  $T_{cs}^*$  is 0.14 whereas they find a value of 0.19 for the surface critical temperature. This has important repercussions for the adsorption isotherms. For example, the temperature  $T^* = 0.16$  lies above  $T_{cs}^*$  in our calculations so the thickness of the film  $h$  grows monotonically with increasing  $n_b/n_{\text{sat}}$ , whereas the same temperature lies below  $T_{cs}^*$  in Ref. 1 so their isotherm exhibits a van der Waals loop at  $T^* = 0.16$  (see Fig. 4 of Ref. 1).

We conclude from this comparison of results that one of the groups has made some numerical errors in their calculations. There are two important differences between the procedures which were employed. First, Teletzke *et al.* solved the relevant integral equation for the density profile of the fluid by converting it to a nonlinear differential equation which was then solved by the Galerkin finite-element method. Our method,<sup>2</sup> which was specifically designed to treat thick films, solves the integral equation by an iterative procedure. Secondly, our procedure<sup>2,7</sup> for locating the wetting transition and determining its order is based on the calculation of  $\gamma(\Gamma)$  and the subsequent determination of the minima of this function. This can be carried out very precisely (see Fig. 2). Teletzke *et al.* do not appear to calculate interfacial free energies but rely on investigation of the shape of the adsorption isotherms. The latter must be determined rather accurately for this procedure to be completely reliable. Indeed it necessitates the accurate calculation of density pro-

files of very thick films close to saturation. We suspect that Teletzke *et al.*'s numerical procedures might run into difficulties in this regime but this requires further investigation. Ideally, a third, independent, group should repeat the calculations and (hopefully!) resolve the issue. While we await the results of further studies, we are presently of the opinion that the wetting transition at a Lennard-Jones 9-3 substrate is always a first-order surface phase transition.<sup>8</sup>

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<sup>1</sup>G. F. Teletzke, L. E. Scriven, and H. T. Davis, *J. Chem. Phys.* **78**, 1431 (1983). We adopt the notation of this paper in the present article.

<sup>2</sup>P. Tarazona and R. Evans, *Mol. Phys.* **48**, 799 (1983).

<sup>3</sup>D. E. Sullivan, *Phys. Rev. B* **20**, 3991 (1979); D. E. Sullivan, *J. Chem. Phys.* **74**, 2604 (1981). In Ref. 1 this approach is termed van der Waals integral theory.

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<sup>5</sup>C. Ebner and W. F. Saam, *Phys. Rev. Lett.* **38**, 1486 (1977).

<sup>6</sup>R. Evans and P. Tarazona, *Phys. Rev. A* **28**, 1864 (1983).

<sup>7</sup>The definition of and the procedure for calculating  $\gamma(\Gamma)$  is described fully in Ref. 2.

<sup>8</sup>It is, of course, possible that choices of free-energy functional different from that employed here, or the incorporation of fluctuation corrections, could affect the order of the wetting transition, but we think that this is unlikely except, perhaps, when  $T_{cw}$  is very close to the bulk critical temperature. We believe that the argument given in Sec. II C of Ref. 2 lends strong support to this viewpoint. Recent calculations [M. P. Nightingale, W. F. Saam, and M. Schick (*Phys. Rev. Lett.* **51**, 1275 (1983))] for a solid-on-solid model, which include fluctuation corrections, also predict that long-range, inverse-power law potentials will always give rise to a first-order transition.

## Reply to "A Comment on the order of the wetting transition at a solid-fluid interface"

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We have independently repeated the calculations of Teletzke *et al.*<sup>1</sup> that are challenged by Evans and Tarazona.<sup>2</sup> The disputed results are adsorption isotherms given by van der Waals' integral theory with an exponential fluid potential and either an exponential fluid-solid potential or a Lennard-Jones 9-3 fluid-solid potential. The adsorption isotherms, calculated by Teletzke *et al.* by means of finite element analysis with a fixed basis, were in turn used to deduce the order of the wetting transition. In this note we choose an adaptive finite element procedure<sup>3</sup> which controls solution error by concentrating basis functions in regions of high curvature of the density profile, i.e., in the solid-fluid interface and the fluid-fluid interface on the other side of the thick film.

We find a substantial departure from the results of Teletzke *et al.* as temperature is decreased and the film thickens. The qualitative difference from the results of Evans and Tarazona gave the prediction of a second-order transition when in fact first order prevails; this we traced to an error in implementing a standard approximation (cf. Appendix A of Ref. 4) to the equation  $d^2u/dx^2 = G[u(x),x]$ . The approximation consists of also expanding the forcing function  $G$  in the finite element basis  $\{\psi_j\}: G = \sum G_j \psi_j(x)$ . This was not done correctly in the code which generated the results of Sec. II of Ref. 1. In addition, at low temperatures the fluid interface narrows and its density profile sharpens, so that the fixed basis set employed by Teletzke *et al.* becomes inefficient, i.e., a large basis on a fine mesh must be used in calculating the thickening film accurately.

We adopt the notation used previously<sup>1</sup> and present the

correct results, first for the exponential fluid-solid potential

$$u_e(x^*) = -W_{\text{exp}} \exp(-x^*/d), \quad (1)$$

and then for the Lennard-Jones 9-3 potential

$$u_e(x^*) = W_{9,3} \left\{ \frac{1}{45} \left( \frac{d}{x^*} \right)^9 - \frac{1}{6} \left( \frac{d}{x^*} \right)^3 \right\}. \quad (2)$$

When  $W_{\text{exp}} = 0.7$  and  $d = 0.9$ , there is a second-order wetting transition at  $T_{cw} = 0.25$ , which is close to the critical

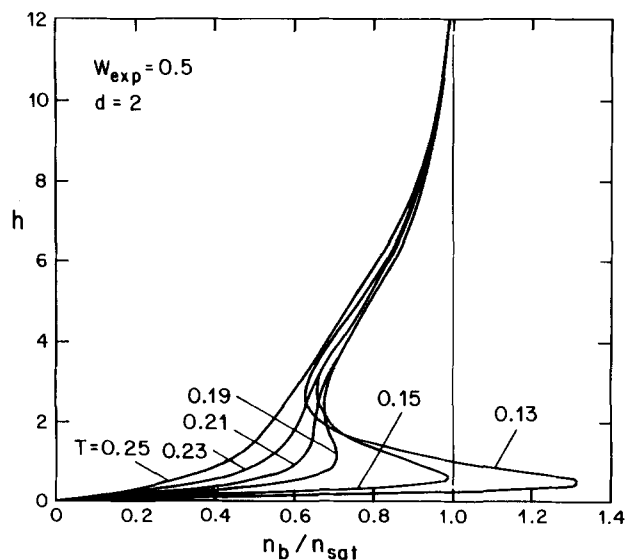


FIG. 1. Adsorption isotherms calculated from van der Waals integral theory with exponential fluid-solid potential and a choice of parameters giving a first-order transition.  $T_{cs} = 0.20$ ,  $T_{cw} < 0.11$  (cf. Fig. 2 of Ref. 1)