Simulation Studies of Wetting on Alkali Metals

Milton W. Cole
Department of Physics
Penn State University
104 Davey Laboratory
University Park, PA 16802 USA

Key words: helium, hydrogen, neon, molecular simulation, liquid-vapor equilibria.

Abstract

A summary is presented of recent simulations of the wetting behavior of simple gases on alkali metals. A specific focus is the nature of the wetting transitions on these surfaces of the gases helium, hydrogen, and neon. Since transitions have been observed experimentally for all of these systems, a principal motivation for performing the simulations is to assess the adsorption potentials which are used in the calculations.

1 Introduction

The concept of the prewetting transition was conceived some twenty years ago, independently by Cahn[1] and Ebner and Saam[2]. The basic idea is that a film has some incentive to adsorb on a surface because of the film-surface attraction, but this incentive may be insufficient to adsorb a thick film because of the free energy cost associated with the interfacial tension. Since the latter falls to zero near the critical point, such a thick film is argued to be inevitable at temperatures sufficiently close to the critical temperature T_c. The transition between nonwetting and wetting occurs

at the wetting temperature T_w. There exist scenarios (depending on the interactions) involving transitions which are either first order or continuous[3]. In the former case, there arises a "prewetting" regime of T in which a coverage discontinuity occurs in an isotherm at a pressure P somewhat below saturated pressure. The prewetting line of such discontinuities $P(T)$ is a two-dimensional analog of the liquid-vapor transition line, both ending with critical points.

Although this prewetting idea was well justified by calculations on model systems[1-5], attempts to observe the transition in the laboratory failed until experimentalists tested[6–8] the explicit predictions of such transitions in ultraweakly adsorbed films on alkali metal surfaces[9–12]. The first such case was that of the ^4He wetting transition on Cs. There is irony in that specific case because ^4He had been assumed to be the universal wetting agent and Cs was "well known" to be a reactive surface! The real situation is that the He-Cs interaction is the least attractive gas-surface interaction in nature! Table 1 presents information about the state-of-the-art theoretical well depths D for this and other weak-binding adsorption potentials[13, 14]. One observes that the value of D in some cases is even smaller than the well depth ϵ of the adsorbate-adsorbate interatomic potential. This weak attraction is logically consistent with nonwetting behavior at low T, so that the only major question concerns the details of the wetting transition. Indeed, a major motivation for simulations discussed here is to test the existing potentials for consistency with existing experiments. A second important motivation is to predict wetting transitions for systems which have not yet been explored experimentally. Other motivations for simulations include the

exploration of issues (such as surface imperfection) which are difficult to evaluate from existing experiments and interest in assessing a simple, heuristic model of Cheng, et al[11]. That model, based on a balance of surface tension σ and adsorption potential V(z) terms, results in an implicit expression for T_w:

$$2\sigma/n = \int dz V(z). \tag{1}$$

Here n is the bulk liquid density at T_w and the integral extends over the domain $z < z_{min}$, the minimum of the potential. This model agrees relatively well with other calculations[15] and makes explicit the Cahn argument that weak potentials have transitions close to T_c. In the case of ^4He, this model predicts too high a value of T_w, relative to the experimental value of 2K[6], leading to a variety of hypotheses to explain the discrepancy[16]. However, the model itself needs to be tested by simulation.

This paper will describe recent simulation studies of helium, hydrogen and neon films on alkali metal surfaces, performed in collaboration with M. J. Bojan, M. Boninsegni, J. K. Johnson, W. A. Steele, and Q. Wang[17-18]. Because the details of these calculations are reported elsewhere, only the principal results will be described here. It should be emphasized that such studies are just beginning and that there remains much more to be done, for both these systems and many other possible cases of wetting transitions.

2 Calculations

The case of ^4He was predicted by a density functional calculation to be nonwetting at $T = 0$ for the surfaces of K, Rb, and Cs[19, 20]. Experiments have since found transitions at Rb near 0.3K[21] and on Cs near 2K; both values are lower than were predicted with Eq. (1). We have performed path integral Monte Carlo (PIMC) calculations for a system of 64 periodically replicated particles on Cs. The results at 1K show the particles to form a droplet, while at 2K the particles are spread nearly uniformly across the surface[17]. Although this behavior is consistent with the experiments, one should be cautious about drawing a conclusion because of the small number of particles and the small dimensions of the simulated box. This deficiency should be remedied in future calculations, which will be quite demanding computationally.

The case of H_2 is one for which Eq. (1) had been found capable of predicting within 10% the wetting temperature on both Rb and Cs[7, 11, 22]. However, our recent simulations have cast doubt on that conclusion[18]. Using the grand canonical PIMC, we have simulated the Rb case, using a potential for which Eq. (1) yields T_w=19K. The actual wetting transition was found with this potential to occur near 26K. We may tentatively conclude that the "true" potential is somewhat more attractive than the one employed in the simulations (by $\sim$ 10%) and that Eq. (1) underestimates the transition temperature for this H_2/Rb case (by $\sim$ 30 %). Neither of these findings is disturbing in view of the uncertainties in their underlying assumptions. In particular, a $\sim$ 40% uncertainty in the potential was estimated in the publication reporting its

derivation; this large uncertainty was described therein as "conservative" [11].

Finally, we turn to the case of Ne wetting Rb and Cs. As seen in Table 1, the relative well depth D/ϵ is particularly small, implying (from Eq. (1)) that the wetting transition ought to occur within a few per cent of T_c [12]. The actual experiments[8] observe wetting on Rb only above 43.4K, i.e., within 1K of T_c. In the case of Ne/Cs, there is evidence of drying behavior close to T_c. Our classical grand canonical MC simulations have been carried out mostly in (periodically replicated) domains of extent $28 \times 28 \times 75\mathring{A}$, which are too small to accurately describe critical fluctuations so close to T_c. When we look in the regime where critical fluctuations do not invalidate the simulation results, $T/T_c < 0.95$, we find nonwetting on these surfaces, a result which is consistent with the data of Hess, et al.[8] When we turn to other (more attractive) cases, e.g., Ne/Li, we do find evidence of wetting transitions. These results are not yet definitive, so they will be described in a future publication.

3 Summary

Our simulations on these surfaces have been able to test both the simple model, Eq. (1), and the existing adsorption potentials. It is reasonable and not surprising that we find deficiencies in both. Comparison with the experimental transition temperature indicates that the He/Cs potential is at least qualitatively consistent with the wetting data. For the case of H_2/Rb, such a comparison implies that the potential is too weakly attractive. Eq. (1) appears to overestimate T_c in the He case and underestimate it in the H_2 case. This contrasting performance evidently bears further scrutiny before

discarding Eq. (1) completely as a predictive relation. In any case, it has at least qualitative applicability.

One should appreciate the immense value of simulations as a means of probing these adsorption potentials. In the contrasting case of moderately or strongly attractive adsorption potentials, a wide variety of experiments can yield information, either direct or indirect, about the potential[23, 24]. In the case of these ultraweak interactions, however, there is a paucity of data so that simulations can play a particularly valuable role. Furthermore, one should recognize that the extraordinary weakness of the interaction implies a special challenge to the theory leading to these potentials. Hence there is particular motivation for future simulations of these systems.

I am grateful to my collaborators in the simulation studies, as well as to many experimentalists for frequent sharing of ideas and data. This research has been support by NSF.

References

[1] J. W. Cahn, J. Chem. Phys. 66 (1977) 3667.

[2] C. E. Ebner and W. F. Saam, Phys. Rev. Lett. 38 (1977) 1486.

[3] V. B. Shenoy and W. F. Saam, Phys. Rev. B52 (1995) 11471.

[4] S. Dietrich, in Phase Transitions and Critical Phenomena, ed. C. Domb and J. L. Lebowitz (Academic, London) Vol. 12 (1988) 1.

[5] J. E. Finn and P. A. Monson, Phys. Rev. A39 (1989) 6402; Y. Fan and P. A. Monson, J. Chem. Phys. 99 (1993) 3003.

[6] P. Taborek and J. E. Rutledge, Physica B197 (1994) 283; K. S.Ketola, S. Wang and R. B. Hallock, Phys. Rev. Lett. 68 (1992) 201; R. B. Hallock, J. Low Temp. Phys. 101 (1995) 31; Bob Evans and Moses Chan, Physics World 9 (1996) 48.

[7] G. Mistura, H. C. Lee and M. H. W. Chan, J. Low Temp. Phys. 96 (1994) 221.

[8] G. B. Hess, M. J. Sabatini and M. H. W. Chan, Phys. Rev. Lett. 78 (1997) 1739.

[9] M. W. Cole, J. Low Temp. Phys. 101 (1995) 25.

[10] J. Treiner, Czech. J. Phys. 46, Suppl. S6 (1996) 2957.

[11] E. Cheng, G. Mistura, H. C. Lee, M. H. W. Chan, M. W. Cole, C. Carraro, W. F. Saam and F. Toigo, Phys. Rev. Lett. 70 (1993) 1854.

[12] E. Cheng, M. W. Cole, S. F. Saam and J. Treiner, Phys. Rev. B48 (1993) 18214.

[13] M. W. Cole, A. Chizmeshya and E. Zaremba, submitted to J. Low Temp. Phys.

[14] M. W. Cole, E. Cheng, C. Carraro, W. F. Saam, M. R. Swift and J. Treiner, Physica B197 (1994) 254; G. Vidali, G. Ihm, H. Y. Kim and M. W. Cole, Surf. Sci. Repts. 12 (1991) 133.

[15] See Refs. 5, 12 and E. Bruno, C. Caccamo and P. Tarazona, Phys. Rev. A35 (1987) 1210.

[16] M. W. Cole, M. R. Swift and F. Toigo, Phys. Rev. Lett. 69 (1992) 2682; J. Dupont-Roc and B. Demolder, J. Low Temp. Phys. 101 (1995) 205; J. E. Rutledge, D. Ross and P. Taborek, J. Low Temp. Phys. 101 (1995) 217; J. Klier and A. F. G. Wyatt, Czech. J. Phys. 46, Suppl S1 (1996) 439.

[17] M. Boninsegni and M. W. Cole, to be published.

[18] M. J. Bojan, M. W. Cole, J. K. Johnson, W. A. Steele and Q. Wang, to be published; M. J. Bojan, M. W. Cole and W. A. Steele, submitted to Phys. Rev. E.

[19] E. Cheng, M. W. Cole, W. F. Saam, and J. Treiner, Phys. Rev. B46 (1992) 13967; Erratum B47 (1993) 14661.

[20] While, in contrast, ^3He is believed to wet all surfaces, it manifests on Cs a prewetting transition below saturated vapor pressure for $T < 0.6K$; see D. Ross, J. A. Phillips and P. Taborek, J. Low temp. Phys. 106 (1997) 81.

[21] A. F. G. Wyatt, J. Klier and P. Stefanyi, Phys. Rev. Lett. 74 (1995) 1151.

[22] D. Ross, J. E. Rutledge and P. Taborek, unpublished.

[23] L. W. Bruch, M. W. Cole and E. Zaremba, Physical Adsorption: Forces and Phenomena (Oxford University Press, Oxford, 1997).

[24] In particular, the absence of diffraction in scattering prevents one from analyzing selective adsorption data to deduce information about the potential; see J. Cui, J. D. White, R. D. Diehl, J. F. Annett and M. W. Cole, Surf. Sci. 279 (1992) 149.

	He (11.0)	Ne (42.25)	H_2 (35.2)	Ar (143.2)
graphite	18	8.2	14	7.3
Au	7.9	6.6	13	6.9
Li	1.5	1.2	2.6	1.7
Rb	0.44	0.33	1.0	0.64
Cs	0.38	0.27	0.82	0.57

Table 1. The ratio of the adsorption potential well depth D to the pair potential well depth ϵ (in parentheses, in Kelvin) for simple gases on various surfaces. Data from Refs. 13 and 14.