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LETTER TO THE EDITOR

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Abstract. We report the observation of a fluctuation-induced first-order phase transition between two states of adsorption at a wall–liquid interface. WDA density functional theory modified to enable input of the measured bulk equation of state is used to confirm the critical nature of the mean-field transition. MD computer simulation results show a first-order phase transition associated with dramatic collective fluctuations in the amount of adsorbed fluid. The qualitative appearance of the large-scale fluctuation events is described.

The physics of first-order phase transitions belonging to the classical van der Waals picture has suffered from the twin disability of the presence of a successful phenomenological theory coupled with a dearth of rigorous knowledge (for a review, see Binder 1987). In contrast, a highly successful theory of the physics of second-order phase transitions has been based on the dominant role played by long-range cooperative phenomena (Wilson and Kogut 1974). Ideally, one would wish for a unified theory of phase transitions, as is indeed suggested by some interpretations of renormalisation group theory (Domany *et al* 1977). Here, one encounters what could be regarded as a third class of phase transitions, which for want of a better term are usually referred to as fluctuation-induced first-order phase transitions. In these cases mean-field theory yields continuous second-order behaviour (i.e. there is no classical spinodal) but the inclusion of fluctuation phenomena results in a first-order transition.

Fluctuation-induced first-order transitions appear most straightforwardly in the context of renormalisation group studies of phenomenological normal mode Hamiltonians; i.e. whenever the first-order behaviour is turned on by the inclusion of fluctuations beyond Landau theory (Domany *et al* 1977, Binder 1987). However, it is much less clear how this phenomenon appears in the context of molecular based Hamiltonians. As steps towards the development of a many-body theory one would like to make progress on the following two aspects: (i) The development of sophisticated mean field theories of molecular systems which are essentially exact apart from the mistreatment of a particular collective mode; i.e. to be certain of the non-existence of a classical spinodal in certain molecular systems. (ii) To obtain unequivocal evidence of fluctuation-induced first-order phase transitions in molecular systems; here, the most direct link with a known many-body Hamiltonian would arise in computer simulation studies. This letter reports recent progress made in both of these directions.

The particular phase transition studied here belongs to a class of interfacial phase transitions known generically as wetting transitions (for general reviews see Sullivan

and Telo da Gama 1986, Fisher 1986, Dietrich 1988). Specifically, we discuss the transition to complete drying by vapour at a wall–liquid interface. The system Hamiltonian, including the substrate field, is defined in terms of square-well interactions. The phase change takes place at bulk liquid–vapour coexistence when the surface field (defined to be the wall–liquid attractive well depth, ε_w) is reduced at fixed temperature T. This transition was the first example of its class to be observed via computer simulation of a many-body Hamiltonian system (van Swol and Henderson 1986). The scope of the simulations reported by van Swol and Henderson (1986) were limited to establishing the principle that wetting transitions are ubiquitous in such systems and can usefully be studied by computer simulation procedures for inhomogeneous fluids. However, at the time the authors were confident that they had observed first-order behaviour, rather than critical drying. Recently, van Swol and Henderson (1989) have made a detailed comparison between these simulation data and a sophisticated coarse-grained density functional theory (hereinafter referred to as WDA theory; Tarazona (1985), Curtin and Ashcroft (1986)). The results of this comparison were surprising in that, although the two methods agreed well deep inside the partial wetting regime, this agreement broke down as ε_w was lowered towards the drying transition. Most strikingly, they even appeared to be in contradiction over the order of the drying transition. However, the comparison of van Swol and Henderson (1989) was incomplete in two significant respects: (i) the WDA theory assumed a modified van der Waals bulk equation of state which meant that in the region of a drying transition it could not accurately model both the wall–vapour and wall–liquid interfaces simultaneously, and (ii) the earlier simulation data were insufficient to rule out a second-order transition on the rapid scale predicted by WDA theory. Accordingly, it was concluded that a full resolution of the problem would require both extensive additional simulations and further development of WDA theory (to enable one to input the known bulk equation of state). This additional work has since been successfully carried out, enabling us to confirm the disagreement over the order and position of the drying transition. Full details of these new results will be published elsewhere. In this letter we focus attention on our observations concerning the role of fluctuation phenomena, as a contribution towards the study of fluctuation-induced first-order phase transitions.

WDA theory denotes a class of mean-field density functionals defined in terms of coarse-grained density profiles ($\bar{\rho}$) and an excess free-energy functional of the form

$$F^{ex}[\bar{\rho}] = \int d1\, \rho(1)[\Delta\psi_{HS}(\bar{\rho}_{HS}(1)) + \Delta\psi_a(\bar{\rho}_a(1))] \tag{1a}$$

$$\bar{\rho}_i(1) \equiv \int d2\, \rho(2)w_i(12, \bar{\rho}_i(1)) \qquad i = \{HS, a\} \tag{1b}$$

where the functions $\Delta\psi$ are excess free energies per particle belonging to a homogeneous fluid (of density ρ), the $w_i(12, \rho)$ are non-local density-dependent weight functions (usually restricted to homogeneous fluid forms) and the subscripts $\{HS, a\}$ imply the use of a bulk equation of state defined in terms of a separation into a hard-sphere term and an attractive interaction term. The choice of weight function is formally defined by the correlation function hierarchy implicit in the free-energy functional (1). To date, most work has concentrated on the hard-sphere contribution, where accurate knowledge of the bulk two-body direct correlation function provides a physically sensible criterion for the choice of hard-sphere weight function. In contrast the attractive interactions have

usually been treated in strict mean-field, apart from by Curtin and Ashcroft (1986) who used inhomogeneous fluid perturbation theory. Such approaches possess a significant drawback when used to study interfacial phase transitions; namely, they enforce an approximate bulk equation of state which in turn perturbs the surface phase behaviour. However, when the free-energy functional is written in the general form (1) it is apparent that the bulk equation of state should really be regarded as a boundary condition. Accordingly, we chose to investigate this approach using various choices for the attractive weight function. The low density result for $w_a(12, \rho)$ is readily derived. However, when this is used in (1) to calculate wet or partially wet wall–liquid density profiles we observed an excessive amount of packing structure. Other choices of weight function showed that WDA theory is sensitive to the nature of $\bar{\rho}_a(1)$, to the extent that unphysical structure is readily generated even for liquid–vapour systems. In happy contrast, we observed far less sensitivity to the choice of bulk equation of state. In particular, for a given bulk liquid density the predicted structure of partially wet wall–liquid interfaces outside the drying region are remarkably insensitive to the choice of $\Delta\psi_a$ when using the strict mean-field result for the attractive weight-function. Our final choice of WDA theory included a simple switch to enable the attractive weight function to change over smoothly to the true weak-gas limit at vapour densities. The bulk equation of state for the isotherm of relevance was available from molecular dynamics (MD) simulation data and the known virial coefficients of square-well fluid (Henderson and van Swol 1985).

Our modified WDA theory described above confirmed the results of van Swol and Henderson (1989) for the structure and free energy of wet and partially wet wall–fluid interfaces, the only benefit here being that we no longer had to shift the temperature to obtain the desired bulk liquid density. Thus, the only significant advance for wetting studies arises from the great improvement in the treatment of the wall–vapour interface corresponding to the correct saturated liquid density. This effect did improve the agreement with simulation data for the contact angle in the middle of the partial wetting regime (see figure 2). However, for our square-well system WDA theory insists on a critical drying transition occurring at a much lower value of ε_w than the transition observed in the simulations. Below we present strong evidence confirming that molecular dynamics simulation yields a first-order drying transition for the isotherm under study. In contrast, combining our improved density functional results with those from van Swol and Henderson (1989), WDA theory implies the total absence of a mean-field spinodal associated with the drying transition (i.e. for all temperatures along the liquid–vapour coexistence curve). Since WDA theory is a sophisticated mean-field theory known to yield very good comparison with simulation data in regions of phase space not strongly influenced by fluctuation phenomena, it follows that the only serious candidate for the discrepancy concerning the position and order of our drying transition is the absence or mistreatment of fluctuation phenomena by WDA theory. Accordingly, we set out to investigate the role played by fluctuation phenomena in our MD simulation system via comparison with WDA theory.

It is noticeable that for liquid–vapour interfaces the comparison between MD and WDA theory is significantly worse than for wet and partially wet wall–liquid interfaces. In fact, the MD profile is much closer to $\bar{\rho}_a(z)$ than to the mean-field profile. A related effect is that the WDA surface tension is significantly higher than that observed in simulation, again in contrast to the situation for wall–liquid interfaces displaying sufficient packing structure. From this, one concludes that the 'free' liquid–vapour profile in our MD simulations is strongly influenced by fluctuation phenomena. Recent theories of critical wetting in $d = 3$ (Fisher and Huse 1985) have concluded that an important
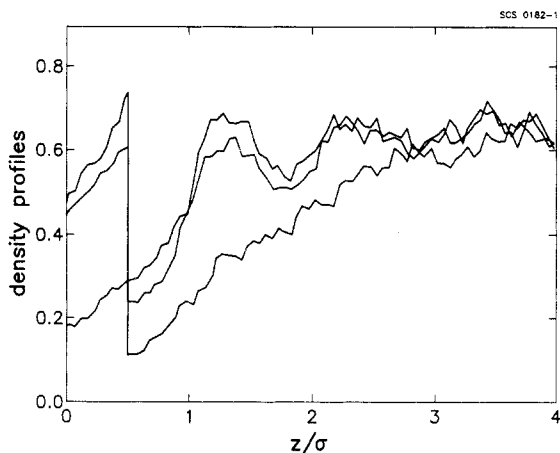
Figure 1. Wall–liquid density profiles at bulk liquid–vapour coexistence for square-well fluid at a square-well wall, in the vicinity of the drying transition at $T^* = 1$. The curves show $\rho(z)\sigma^3$ from a series of three consecutive subaverages of $\frac{1}{2}$ million collisions each, in which a transient large-scale collective fluctuation to a state of low adsorption occurred between states of much higher adsorption; in chronological order, the corresponding adsorptions are $\Gamma\sigma^2 = -0.31$, -0.84 and -0.22, respectively. This particular example forms part of the second series of runs at $\varepsilon_w/kT = 0.95$, referred to in table 1.

measure of the amount of fluctuations is the capillary-wave parameter $\omega \equiv kT/4\pi\gamma_{LV}\xi^2$, where γ_{LV} denotes the liquid–vapour surface tension and ξ is the bulk correlation length (or more precisely, the decay length of the tail of the mean-field density profile; Henderson (1987)). Substituting our values measured by MD and WDA theory we find $\omega \simeq 1.6$ which lies well inside the so-called weak-fluctuation regime; $\frac{1}{2} < \omega < 2$. Despite the name, this conclusion implies that unless finite-size effects intervene we should expect to observe fluctuation phenomena of a non-mean-field character. Alternatively, finite-size dynamics could conceivably be playing an important role in our simulations (Binder 1989). The simulations were carried out at fixed $N = 512$ between walls of area $A = 48.6038\sigma^2$, with σ denoting the square-well repulsive core diameter. The simulation systems were always about half-filled with liquid, which ensured that we remained at 'bulk' liquid–vapour coexistence. The temperature was fixed at kT equal to the fluid–fluid attractive well depth; i.e. $T^* = 1$. In argon units, we were readily able to observe time periods of 1 to 4 ns (up to 16 million collisions). In practice, we found that when a large fluctuation occurred it did so on a much more rapid time scale than this (0.1 to 0.4 ns), but that such events were both rare and unpredictable (apparently chaotic). Thus, although we were not able to take averages over many such events we were able to observe first-order transitions initiated by a single such event. The physical nature of the large collective mode was no doubt influenced by short-wavelength capillary-wave phenomena, but was observed in our simulations as a bodily motion of the liquid film.

The strongest evidence that emerged for the first-order nature of the MD drying transition arose from observations of the profile behaviour during the collapse of a metastable branch of relatively high adsorption. A collective fluctuation typical of the drying transition region is shown in figure 1. Such fluctuations would happen suddenly and occur sparsely; in a metastable run of 4 million collisions we typically observed one such dramatic fluctuation and this would involve only about $\frac{1}{2}$ million collisions. The

Table 1. Simulation data for the $T^* = 1$ metastable branch. ε_w is the surface field parameter. MCOLLS denotes the number of collisions attributed to a metastable state (excluding a one million equilibration period); i.e. prior to an observed collapse to a completely dry wall. Γ denotes adsorption at the wall–liquid interface; the results show averages over 4 million collisions collected in 8 equal subaverages occurring sequentially within a metastable or stable regime.

ε_w/kT	MCOLLS/10^6	$\Gamma\sigma^2$
0.85	<0.5	—
0.875	16.5	-0.38 ± 0.06
0.90	1.5	—
0.925	11.0	-0.38 ± 0.10
0.95	>9.2	-0.41 ± 0.06
0.95	>4.0	-0.36 ± 0.08
0.97	>5.5	-0.36 ± 0.04

onset of such an excursion by the liquid film and the manner of any subsequent return to the wall were strikingly sudden and very sensitive to initial conditions; i.e. suggestive of chaotic disturbance by occasional wild events. If a configuration of a system showing apparently stable partial wetting behaviour is used as the starting point for a new simulation at a lower value of ε_w, then three different regimes are encountered. (i) If the new value of the surface field is much lower than the drying transition point then the liquid film smoothly detaches itself from the wall and moves rapidly away, eventually colliding with the far side of the simulation box (which in our case is a hard wall). (ii) If the surface field parameter lies relatively close to but below the drying transition, then one observes occasional large-scale fluctuations in the position of the liquid film (as described above), one of which ultimately goes too far for the system to be able to recover. (iii) Above the apparent drying transition point, collective fluctuations of the type seen in regime (ii) are still observed although somewhat masked by a decreasing amplitude. A summary of our simulation data focusing on the density profile behaviour is presented in table 1. From these observations we conclude that in our square-well system at $T^* = 1$ there is a first-order transition at $\varepsilon_w = 0.93 \pm 0.02$. Not shown in table 1 are observations that indicate that the $\varepsilon_w = 0.925$ system lies very close to the drying transition point (these details will be published elsewhere).

Our MD surface tension data are consistent with the position and order of the drying transition as observed from the order-parameter behaviour, but this is of little corroborative value because direct measurement of interfacial free energy is plagued by large statistical error. A much more accurate measurement can be made of the derivative of the free energy with respect to the surface field parameter, using the surface 'magnetisation' sum rule; equation (11) of van Swol and Henderson (1986). Thus, if one is prepared to accept the position of the drying transition as observed from the profile behaviour then the surface 'magnetisation' sum rule data can be integrated to obtain the variation of the contact angle with ε_w. Figure 2 shows the result of this analysis, in comparison with the prediction of WDA theory.

This letter has reported results supporting the observation of a fluctuation-induced first-order phase transition within a many-body Hamiltonian system. The interfacial nature of the transition, pinned by the presence of a substrate, leads to sufficiently dramatic changes in the one-body order parameter to enable study by MD computer
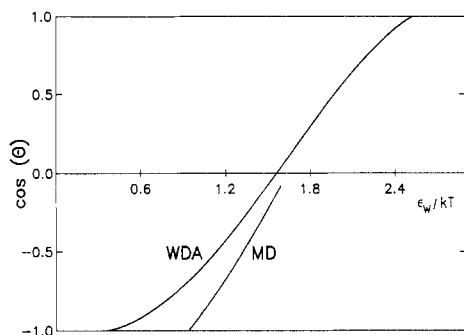
Figure 2. Cosine of the contact angle versus surface field strength for the isotherm $T^* = 1$. WDA theory yields critical drying whereas MD simulation data imply a first-order drying transition at a significantly higher value of the surface field parameter.

simulation procedures. In particular, large-scale collective fluctuations of the amount of adsorbed fluid were directly obseryed. The non-existence of a mean-field spinodal associated with the transition was implied by a sophisticated density functional theory that, in the absence of collective fluctuations, is capable of accurate simultaneous descriptions of wall–liquid and wall–vapour interfaces in the presence of a specified bulk equation of state.

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