PHYSICAL REVIEW E VOLUME 51, NUMBER 3 MARCH 1995

Wetting on lines and lattices of cylinders

W. R. Osborn and J. M. Yeomans
Department of Physics, Oxford University, Oxford OX1 3NP, England
(Received 14 January 1994)

This paper discusses wetting and capillary condensation transitions on a line and a rectangular array of cylinders using an interface potential formalism. For a line of cylinders, there is a capillary condensation transition followed by complete wetting if the cylinders are sufficiently close together. Both transitions disappear as the cylinder separation is increased. The dependence of the wetting phase diagram of a rectangular array of cylinders is discussed as a function of the chemical potential, substrate-fluid interaction strength, and surface tension.

PACS number(s): 68.45.Gd, 47.55.Mh

I. INTRODUCTION

The wetting of planar surfaces is now well understood [1–3]. However, in many realistic situations, substrates are far from planar. A particularly important example is provided by porous media, whose wetting properties have implications for fluid flow [4], oil recovery [5], and also the probing of the fractal geometry of surfaces [6]. Our aim in this paper is to describe wetting and capillary condensation on lines and arrays of cylinders as a step towards understanding the properties of binary fluids in complicated geometries.

For such complicated geometries rigorous theoretical methods quickly become intractable and approximations must be made. A profitable approach has been to use an interface potential which replaces the density profile at a fluid-fluid interface by a sharp kink and uses a local surface tension [1,3]. This approach is valid far from the bulk critical point and for wetting layers thicker than a few intermolecular spacings. It has the advantage that it is easily implemented yet provides qualitatively correct phase diagrams.

Cheng and Cole [7] and Napiórkowski, Koch, and Dietrich [8] applied the interface potential approach to wetting in a corner, Darbellay and Yeomans [9] to wetting in a slit, and Robbins, Andelman, and Joanny [10] to wetting on a line of slits. Dobbs, Darbellay, and Yeomans [11] extended the approach to treat two spheres and subsequently a square array of cylinders [12] in both the grand canonical and the more physically realistic canonical ensembles. In each case, sensible qualitative results were obtained for the phase behavior, although, as one might expect, subtle details of the interface position are not given correctly [3].

In Sec. II we use such an interface potential approach to study wetting on a line of cylinders. We consider the case of van der Waals interparticle interactions. If the cylinders are close enough together for a capillary condensation transition to occur, the system undergoes complete wetting as liquid-gas coexistence is approached. Otherwise, the cylinders behave individually rather than collectively and the wetting transition is suppressed.

In Sec. III a rectangular array of cylinders is considered. The phase diagram is determined as a function of the aspect ratio of the array, the chemical potential, the strength of the van der Waals interactions, and the surface tension. Limiting cases in which this substrate reverts to the line of cylinders described in Sec. II and the square array considered by Dobbs and Yeomans [12] are discussed.

These problems have been addressed in the past using an approximation in which all interfaces are assumed to be circular with curvature proportional to the chemical potential [13,14]. This is exactly the limit of zero van der Waals interaction. In Sec. IV we relate our results to this work by discussing the changes in the phase diagrams which result first from including a wetting layer of nonzero thickness and second from relaxing the condition of nonconstant interface curvature.

Our results are summarized in Sec. V.

II. AN INFINITE LINE OF CYLINDERS

First we consider wetting on an infinite line of identical cylinders lying along the x axis with their axes parallel to the z axis, as shown in Fig. 1. The cylinders have radius r_0 and their separation is L'. The relevant part of the grand potential per cylinder, per unit length in the z direction, is taken to be

$$\Phi = 4\left(\int_0^{+L'/2}\left\{\sigma\sqrt{1+l_x^2(x)}+\widetilde{\Delta\mu}\left(l(x)-\frac{\pi r_0^2}{2L'}\right)\right\}dx + W[l(x)]\right), \tag{1}$$

where $l(x)$ is the interface position and the subscript x denotes differentiation with respect to x.

The first term in Eq. (1) is the free energy of the liquid-gas interface, the surface tension σ multiplied by the surface area. The second is a bulk term due to the excess cost of the adsorbed, unfavorable liquid. If ρ_l and ρ_g are

1063-651X/95/51(3)/2053(6)/$06.00

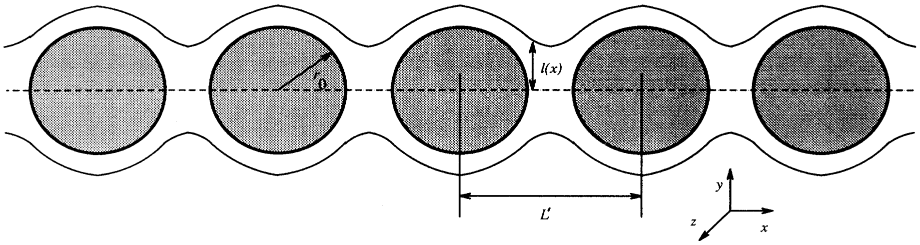


FIG. 1. Arrangement of fluid around a line of cylinders for a bridged phase.

the liquid and gas number densities, respectively, then the free energy per unit volume of the liquid phase over and above that of the gas phase is

$$\widetilde{\Delta\mu} = (\mu_c - \mu^*)(\rho_l - \rho_g), \tag{2}$$

with μ^* the chemical potential of the fluid in the system and μ_c the chemical potential at bulk liquid-gas coexistence.

The final term models the interparticle interactions which, for nonretarded van der Waals forces, can be written

$$W[l(x)] = \int_0^{+L'/2} \int_{l(x)}^{\infty} \Pi(x', y(x'), r_0, L')\, dy\, dx' \tag{3}$$

with a disjoining pressure

$$\Pi(x, y, r_0, L') = \sum_i \int_{\text{cylinder}\, i} \frac{W_0'}{|\mathbf{r} - \mathbf{r}'|^6} d\mathbf{r}' \ , \tag{4}$$

where the summation is taken over all cylinders i. Note that the integrals in Eqs. (3) and (4) are over the gas and the substrate; all other interactions are either independent of $l(x)$ or can be reformulated as integrals over these regions. The strength of the interactions is $W_0' = A/\pi^2$, where A is the conventionally defined Hamaker constant.

The integral in Eq. (4) cannot be performed analytically, in contrast to the cases of a spherical substrate [15] and a cylindrical pore [16], but the numerical result is well fit by a function

$$\Pi(x, y, r_0, L') \approx W_0' \sum_{i=-\infty}^{\infty} \left(\frac{\pi e^{-(l_i/r_0 - 1)}}{6(l_i - r_0)^3} + \frac{3\pi^2 r_0^2}{8 l_i^5} \right), \tag{5}$$

where l_i is the distance from the centre of cylinder i to the point $\mathbf{r}$. The first term in expression (5) is accurate at small distances from a cylinder, when the substrate acts like a flat plane. The second gives the correct behavior in the long distance limit. The fit (5) agrees with numerical integration of the disjoining pressure to within 10%, with the largest discrepancy occurring in the crossover region, at a distance of about r_0 from the surface of a cylinder. This discrepancy is unimportant because the contribution of the interactions to the total free energy is small compared to that of the surface energy at this distance.

The grand free energy Φ can be minimized with respect to $l(x)$ using the Euler-Lagrange formula, yielding a nonlinear differential equation

$$\frac{d}{dx} \left(\frac{\sigma l_x}{\sqrt{(1 + l_x^2)}} \right) - \widetilde{\Delta\mu} + \Pi(x, l(x), r_0, L') = 0. \tag{6}$$

A solution where the liquid forms bridges between the cylinders (see Fig. 1) may be found if this is solved with boundary conditions $l_x = 0$ at $x = 0$ and $x = L'/2$.

To find the unbridged solution, where the interface wraps around each individual cylinder, it is necessary to formulate problem in polar coordinates with the origin at the centre of a cylinder. The Euler-Lagrange minimization then gives

$$\frac{d}{d\theta} \left(\frac{\sigma l_\theta}{\sqrt{(l^2 + l_\theta^2)}} \right) - \widetilde{\Delta\mu}\, l(\theta)$$

$$+ \Pi(\theta, l(\theta), r_0, L') l(\theta) - \frac{\sigma l(\theta)}{\sqrt{(l^2 + l_\theta^2)}} = 0. \tag{7}$$

The boundary conditions are $l_\theta = 0$ at $\theta = 0$ and $\pi/2$, where $l_\theta \equiv dl(\theta)/d\theta$.

The solutions to the differential equations (6) and (7) can be found numerically using a relaxation method for different values of the dimensionless parameters $\mu = \widetilde{\Delta\mu} r_0/\sigma$, $L = L'/r_0$, and $W_0 = W_0'/(\sigma r_0^2)$. Once the interface profiles are known, the grand free energy of each phase can be calculated from Eq. (1) using numerical integration techniques, allowing comparison of the free energies and determination of the stable configuration.

The resulting phase diagram is shown in Fig. 2. For $L < 2$ the cylinders are overlapping and the problem is not defined. The unbridged phase is stable at large μ, as expected. For $2 < L < L_c(W_0)$, as μ is decreased, there is a first-order phase transition to the bridged phase and then, as $\mu \to 0$, the interface unbinds to infinity, an example of a complete wetting transition. As the surface unbinds to large distances, it becomes flat and it follows from (5) and (6) that

$$\widetilde{\Delta\mu} \sim \frac{\pi^2 r_0^2 W_0'}{2L' l^4} \quad \text{as } l \to \infty. \tag{8}$$

This shows that the line of cylinders is behaving, as expected, like a plate of effective thickness $\pi r_0^2/L'$.

For $L > L_c$, capillary condensation does not occur as

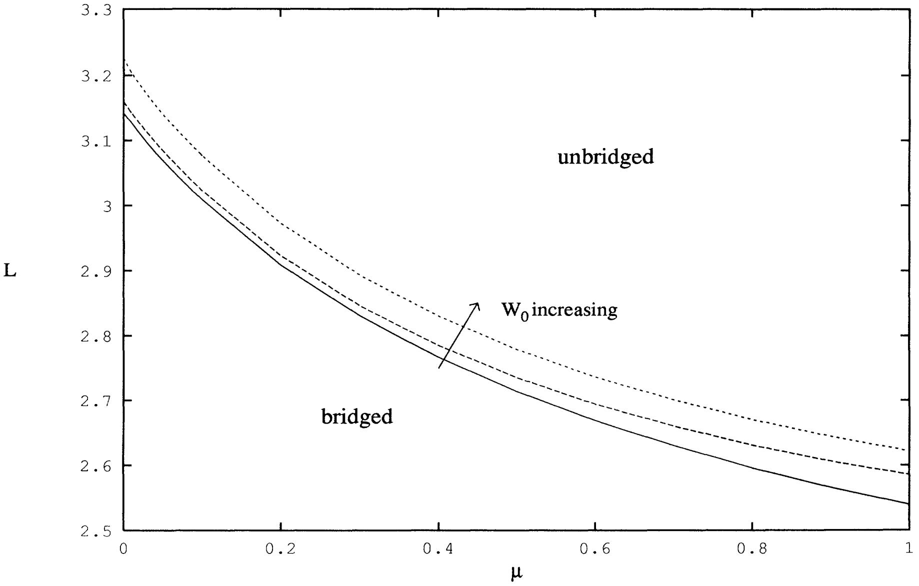


FIG. 2. Dependence of the bridging transition of a single line of cylinders on the reduced van der Waals interaction W_0: solid line, $W_0 = 0$; long-dashed line, $W_0 = 2.5 \times 10^{-6}$; short-dashed line, $W_0 = 2.5 \times 10^{-4}$.

μ decreases and the complete wetting transition is suppressed by the substrate geometry. For vanishingly small W_0 at $\mu = 0$, the surface area is the only relevant quantity. The liquid-gas surface area per unit length for a single cylinder in the unbridged phase is $2\pi r_0$, while that of a bridged film is $2L_c r_0$, giving $L_c(0)=\pi$ in agreement with the numerical solution.

As W_0 is increased at fixed μ, the interfaces lie further from the substrates. For an approximately flat, bridged interface the surface energy is virtually unchanged by this. However, for the unbridged solution the surface area and hence the surface energy must increase as the interface moves. Thus the unbridged solution becomes less favorable for a given μ, as seen in Fig. 2.

III. AN INFINITE RECTANGULAR ARRAY OF CYLINDERS

An infinite number of lines of cylinders can be brought together to produce a rectangular array with interline distance D', as shown in Fig. 3. As $D = D'/r_0$ is reduced, this system shows a crossover from the behavior of a line of cylinders to that reported in Dobbs and Yeomans [12] for a square array.

Two new phases might be expected to exist. The first of these consists of bridging between lines of cylinders as well as between the cylinders in one line. To find such a doubly bridged solution it is necessary to use a polar coordinate system centered on an interstitial site such as point A in Fig. 3. The Euler-Lagrange minimization then gives

$$\frac{d}{d\theta}\left(\frac{\sigma l_\theta}{\sqrt{(l^2+l_\theta^2)}}\right)+\widetilde{\Delta\mu}\,l(\theta) -\Pi(\theta',l(\theta'),r_0,L')l(\theta)-\frac{\sigma l(\theta)}{\sqrt{l^2+l_\theta^2}}=0, \tag{9}$$

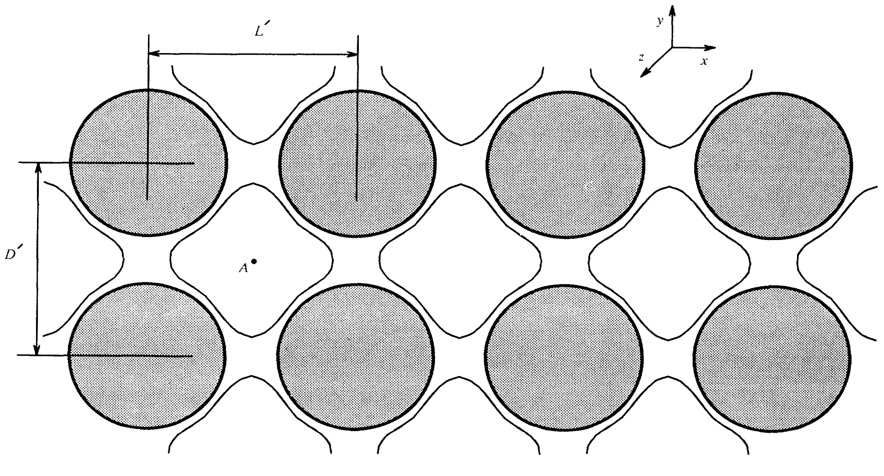


FIG. 3. Part of a rectangular array of cylinders, showing the doubly bridged phase.

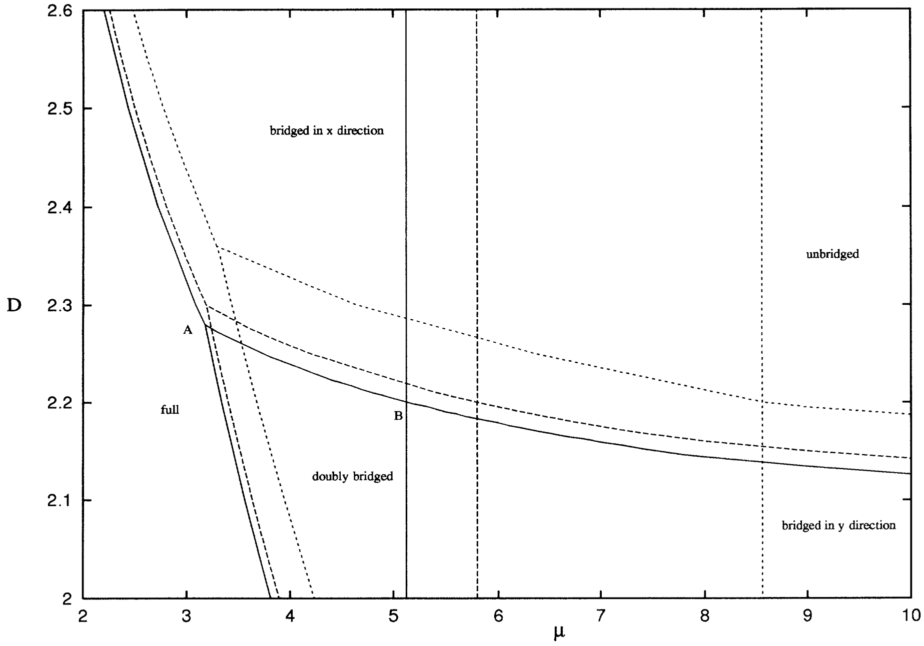


FIG. 4. Phase diagram of an array of cylinders with $L = 2.2$ for three values of W_0: solid line, $W_0 = 0$; long-dashed line, $W_0 = 2.5 \times 10^{-6}$; short-dashed line, $W_0 = 2.5 \times 10^{-4}$. The results are derived from solutions to Eqs. (6) and (7). For $W_0 = 0$ the simple model described in Sec. IV gives identical results.

where l' and θ' are the distance and angle to point (l,θ) from the center of one of the four nearest cylinders. The boundary conditions are $l_\theta = 0$ at $\theta = 0$ and $\theta = \pi/2$. Equation (9) is solved numerically, as before.

There is also a phase where the space between the cylinders is completely filled with liquid. The free energy of this per cylinder, per unit length in the z direction is

$$\Phi_{\text{full}} = \widetilde{\Delta\mu}(L'D' - \pi r_0^2). \tag{10}$$

From comparisons of the free energies, the stable configuration can be found for given values of the four parameters $L, D, \mu = \widetilde{\Delta\mu} r_0/\sigma$, and $W_0 = W_0'/\sigma r_0^2$.

Phase diagrams are plotted in Figs. 4 and 5 and are discussed below.

(i) Small L. Figure 4 shows a cross section through the phase diagram for $L = 2.2$ and $W_0 = 2.5 \times 10^{-6}$. For any finite D, the behavior is no longer that of many separate horizontal lines of cylinders. Complete wetting at $\mu = 0$ is replaced by a transition to a full phase at $\mu > 0$. For large D, this transition lies along the line $D = 2/\mu$. As D decreases, the phase which is singly bridged along the $\hat{\mathbf{x}}$ direction becomes unstable, as expected, and the doubly bridged solution is favored. For $D = L = 2.2$, symmetry

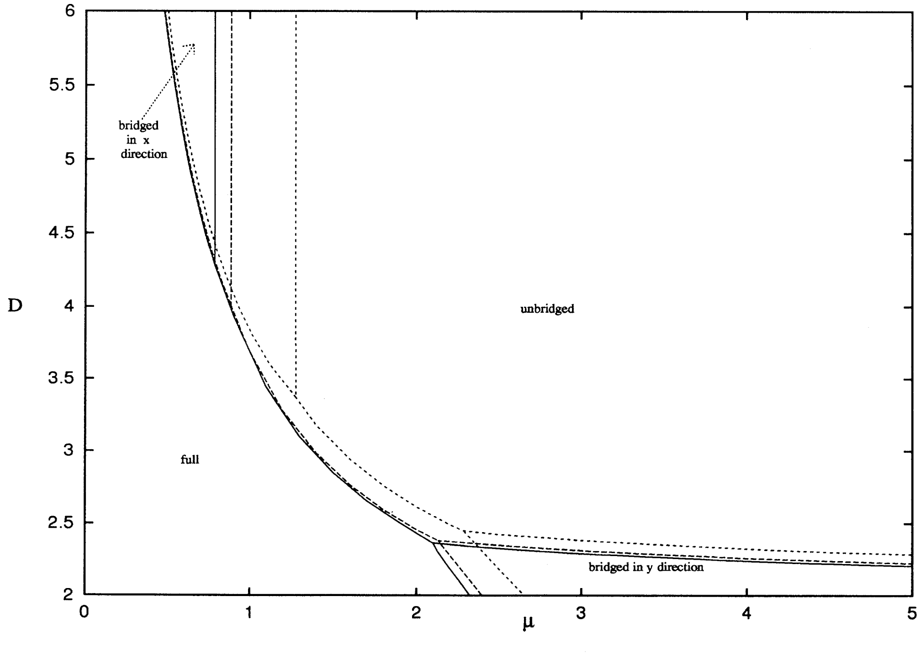


FIG. 5. Phase diagram of an array of cylinders with $L = 2.6$ for three values of W_0: solid line, $W_0 = 0$; long-dashed line, $W_0 = 2.5 \times 10^{-6}$; short-dashed line, $W_0 = 2.5 \times 10^{-4}$.

demands that singly bridged solutions cannot be stable and the theory reduces to that of Dobbs and Yeomans for a square array [12]. For $D < L$, as μ is decreased, the system jumps from being unbridged to singly bridged along $\hat{\mathbf{y}}$ to doubly bridged to full, the order of increasing liquid volume.

As W_0 is increased the transitions occur at larger values of both D and μ. The dominant effect is for the increased disjoining pressure to push the interface away from the cylindrical substrate, so increasing its length and surface energy. Thus, those phases with more interface near a cylinder become relatively less favored, allowing the full region to grow at the expense of the bridged and the bridged at the expense of the unbridged phase.

As de Gennes [17] has pointed out, $l = \sqrt{W_0'/\sigma}$ is a length that sets the scale for competition between surface tension and van der Waals effects. For the parameters used here, $l/r_0 \sim 10^{-2}$–10^{-3} is small compared to unity. Therefore we do not expect the van der Waals term to have a strong qualitative effect on the shape of the phase diagram. However, rather large quantitative changes are seen.

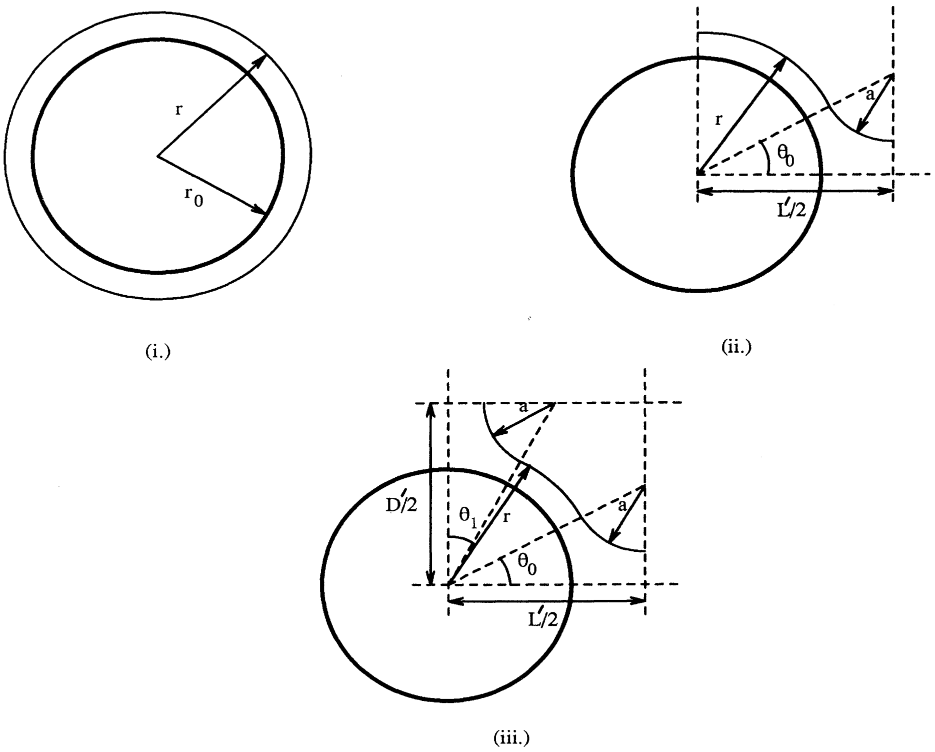
(ii) Increasing L. For $L = 2.6$ and $W_0 = 2.5\times10^{-6}$, the phase diagram is that shown in Fig. 5. As L is increased, the quadruple point B in Fig. 4 moves to lower values of μ until it coincides with point A, when the doubly bridged phase disappears from the phase diagram. Moreover, the phase which is singly bridged along $\hat{\mathbf{x}}$ is stable only at increasingly high values of D as L is increased further until $L \equiv L_c^*$, when it becomes thermodynamically unstable for all D. L_c^* is, as expected, approximately equal to L_c, the critical value above which a line of cylinders does not undergo complete wetting, with small corrections due to the influence of the other cylinders in the array.

IV. A SIMPLE MODEL

The interface potential approach already involves considerable approximation. However, it still relies on the high symmetry of the system considered to produce tractable, one-dimensional, nonlinear differential equations. To better model porous media it would be desirable to be able to treat more complicated substrate geometries. Thus we now consider a much simpler way of modeling the phases in the cylindrical array and compare the resulting phase diagrams with those obtained from the interface potential approach. We find only small discrepancies for physically realistic W_0, giving confidence that the simpler model will give qualitatively correct phase diagrams for more realistic models of porous media.

The approach is to approximate the interface shapes in the different thermodynamically stable phases by simple curves that can be handled analytically. The effect of the van der Waals interaction is incorporated by assuming that where an interface wraps around a cylinder it lies a distance r from the center of the cylinder, where r follows from the flat plane result

$$r - r_0 = \left(\frac{W_0'\pi}{6\widetilde{\Delta\mu}}\right)^{1/3} . \tag{11}$$



(i.)

(ii.)

(iii.)

FIG. 6. Approximate geometries used to model the interface position in the approach described in Sec. IV: (i) unbridged phase, (ii) bridged phase, (iii) doubly bridged phase. $a = r_0/\mu$.

Where the liquid forms bridges between cylinders, the bridges are taken to have a radius of curvature $a = \sigma/\widetilde{\Delta\mu} \equiv r_0/\mu$, which follows from minimizing the free energy of a bridge with respect to a. By assuming that the arcs of radius r and a meet tangentially, the interface shape is completely defined.

The different phases can be modeled as shown in Fig. 6.

(i) The unbridged phase consists of a circle of radius r, centered on a cylinder.

(ii) The singly bridged phase consists of an arc of radius r, centered on a cylinder, for $\theta > \theta_0$, with θ measured from the direction of bridging, and an arc of radius a tangential to this at $\theta = \theta_0$, with $\partial l/\partial x = 0$ at $x = L'/2$, where $\cos\theta_0 = L'/2(r + a)$.

(iii) The doubly bridged phase consists of an arc of radius r, centered on a cylinder, for $\theta_0 < \theta < \theta_1$, and two arcs of radius a tangential to this, the first at $\theta = \theta_0$ with $\partial l/\partial x = 0$ at $x = L'/2$, where $\cos\theta_0 = L'/2(r + a)$, and the second at $\theta = \theta_1$ with $\partial l/\partial y = 0$ at $y = D'/2$, where $\cos\theta_1 = D'/2(r + a)$.

The grand free energy is taken to be

$$\Phi = \sigma \times (\text{interface area}) + \widetilde{\Delta\mu} \times (\text{fluid volume}). \quad (12)$$

For $r = r_0$, corresponding to $W_0 = 0$, this approach is exact and was first described for an array of cylinders by Princen [13]. The results correspond to the solid curves in Figs. 4 and 5. If the simple model described by Eqs. (11) and (12) and depicted in Fig. 6 is used, agreement with the free energies calculated using the interface potential approach is found to within 0.5% and 2% for $W_0 = 2.5 \times 10^{-6}$ and 2.5×10^{-4}, respectively. This leads to phase boundaries which are typically shifted $\approx 75\%$ of the way from the $W_0 = 0$ results towards those obtained by the interface potential approach.

V. DISCUSSION

In this paper we have described wetting on a line and rectangular array of cylinders. For a line of cylinders a capillary condensation or bridging transition is followed by complete wetting as $\mu \to 0$. If the cylinders are sufficiently far apart, bridging does not occur and the wetting transition is suppressed: the cylinders are now behaving individually rather than as an effectively planar substrate.

For an array of cylinders we have calculated the phase diagram as a function of the aspect ratio and reduced chemical potential. Several different capillary condensation transitions occur: to states bridged in the $\hat{\mathbf{x}}$ or $\hat{\mathbf{y}}$ directions, to a doubly bridged phase, or to a phase where the liquid completely fills the volume between the cylinders.

The thin-thick transitions which correspond to wetting on a cylindrical substrate [15,18] are not included in this model where we consider an effective interface potential with a single minimum. The results of Dobbs and Yeomans [19] for adjacent spheres indicate that including retarded van der Waals terms in the potential to model such transitions would not substantially affect capillary condensation, while the thin-thick transition lines would essentially follow those for an individual cylinder.

The phase diagrams have also been obtained using an interfacial potential approximation which treats the interface as a sharp delineation between the two phases. The interface position is obtained as the solution of a nonlinear differential equation. This has allowed us to test a simpler approach where the shape of the interface in each phase is fed in as an assumption. The results agree very well with those obtained by the interface potential method, but only when a wetting layer around each cylinder is included in the model.

ACKNOWLEDGMENTS

It is a pleasure to thank H. T. Dobbs and J. O. Indekeu for many useful discussions. W.R.O. acknowledges support from the EPSRC and British Gas plc and J.M.Y. from EPSRC.

---

[1] M. Schick, in *Liquids at Interfaces*, Les Houches Session XLVIII, edited by J. Charvolin, J. F. Joanny, and J. Zinn-Justin (North-Holland, Amsterdam, 1990).

[2] D. E. Sullivan and M. M. Telo da Gama, in *Fluid Interfacial Phenomena*, edited by C. A. Croxton (Wiley, New York, 1986).

[3] S. Dietrich, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and J. Lebowitz (Academic, London, 1988), Vol. 12.

[4] D. Wilkinson, in *Mathematics in Oil Production*, edited by S. Edwards and P. R. King (Clarendon, Oxford, 1988).

[5] E. J. Hinch, in *Mathematics in Oil Production* (Ref. [4]).

[6] P. Pfeifer and M. W. Cole, New J. Chem. **14**, 221 (1990).

[7] E. Cheng and M. W. Cole, Phys. Rev. B **41**, 9650 (1990).

[8] M. Napiórkowski, W. Koch, and S. Dietrich, Phys. Rev. A **45**, 5760 (1992).

[9] G. A. Darbellay and J. M. Yeomans, J. Phys. A **25**, 4275 (1992).

[10] M. O. Robbins, D. Andelman, and J. F. Joanny, Phys. Rev. A **43**, 4344 (1991).

[11] H. T. Dobbs, G. A. Darbellay, and J. M. Yeomans, Europhys. Lett. **18**, 439 (1992).

[12] H. T. Dobbs and J. M. Yeomans, Mol. Phys. **80**, 877 (1993).

[13] H. M. Princen, J. Colloid Interface Sci. **30**, 69 (1969).

[14] G. Mason and N. R. Morrow, J. Colloid Interface Sci. **100**, 519 (1984).

[15] M. P. Gelfand and R. Lipowsky, Phys. Rev. B **36**, 8725 (1987).

[16] M. W. Cole and W. F. Saam, Phys. Rev. Lett. **32**, 985 (1974).

[17] P. G. de Gennes, in *Physics of Disordered Materials*, edited by D. Adler *et al.* (Plenum, New York, 1985).

[18] P. J. Upton, J. O. Indekeu, and J. M. Yeomans, Phys. Rev. B **40**, 666 (1989).

[19] H. T. Dobbs and J. M. Yeomans, J. Phys. Condensed Matter **4**, 10 133 (1992).