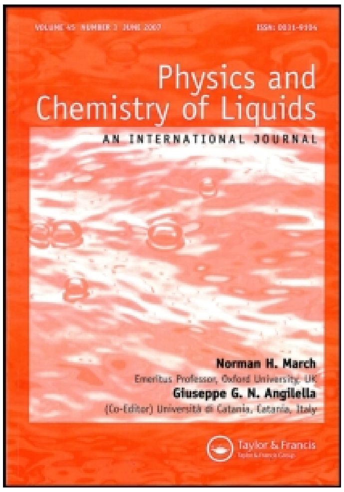

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A Unified Theory of Adsorption and Wetting Using the Percus Yevick Equation for Hard Spheres with Surface Adhesion

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The recent analysis by Baxter of the Percus-Yevick model for an assembly of similar spherical particles with hard sphere repulsion plus a delta function attraction is generalised to an arbitrary number of components. We use the solution to study one component gas adsorption onto a planar substrate. The resulting adsorption isotherms exhibit monolayer or multilayer wetting according to the strengths of the interaction parameters. In particular, we find that multilayer wetting will not occur if the adsorbate/adsorbate interaction is sufficiently weak regardless of the strength of the adsorbate/adsorbent interaction. For weak adsorbate/adsorbate interactions at low gas pressures the adsorption saturates at approximately a monolayer as the adsorbate/adsorbent interaction is increased.

1 INTRODUCTION

In a recent paper[1] we have studied physical adsorption using a very simple model based in part on the mean spherical model (MSM) and hard sphere Percus-Yevick (HSPY) approximations. The results obtained described qualitatively some aspects of gas adsorption at high pressures and high temperatures. However the approximations involved were not adequate to yield multilayer wetting. Clearly a better model which can handle the correlations induced by attractive interactions is needed. It is now known that for a one component system the PY approximation does predict a first order gas-liquid transition when attractive interactions are included. This result first became apparent from numerical studies.[2-5] However later an analytic solution to the P–Y equations was obtained for the particular case of a potential consisting of a hard core plus a delta function attraction.[6] (We refer to this as the sticky sphere Percus-Yevick (SSPY) approximation.) The solution for the isotherms obtained via the compressibility relation closely resembled those for the familiar van der Waals fluid. In view of this success it seems reasonable that generalising the model to incorporate adsorption may yield multilayer wetting.

In this paper it will be shown that the SSPY model can indeed yield multilayer wetting under certain conditions and that the isotherms resemble some of those originally labelled by Brunauer Emett and Teller.[7] The paper is set out as follows. In the next section we generalise our earlier work to incorporate the SSPY approximation. Our method parallels recent work by Perram and Smith[8] who studied in detail the simplest multicomponent SSPY model namely a two component one with equal diameters in the limit that only like atoms interact attractively. Section 3 reviews those results obtained for the one component system which are essential for the case of adsorption. An expression for the adsorption isotherm is derived and studied in detail in Section 4. We close with a brief discussion.

2 THE SSPY APPROXIMATION FOR MULTI-COMPONENT SYSTEMS

We consider initially an assembly of spherical particles consisting of species α, β, γ ... with number densities ρ_α, ρ_β, ρ_γ ... and hard sphere radii R_α, R_β, R_γ.... The total correlation function $h_{\alpha\rho}$ is related to the direct correlation function $\mathbf{c}_{\alpha\beta}$ via the Ornstein-Zernike relation

$$h_{\alpha\beta}(\mathbf{r}) = \mathbf{c}_{\alpha\beta}(\mathbf{r}) + \sum_\gamma \rho_\gamma \int ds\, \mathbf{c}_{\alpha\gamma}(\mathbf{s}) h_{\gamma\beta}(|\mathbf{r} - \mathbf{s}|). \tag{1}$$

It is convenient to take the three dimensional Fourier transform of Eq. (1) defined as follows:

$$[\tilde{\mathbf{f}}]_{\alpha\beta} = \sqrt{\rho_\alpha \rho_\beta} \int e^{ik\cdot r} f_{\alpha\beta}(\mathbf{r}) d\mathbf{r}. \tag{2}$$

We then obtain from Eqs. (1) and (2)

$$[\mathbf{I} + \tilde{\mathbf{h}}][\mathbf{I} - \tilde{\mathbf{c}}] = \mathbf{I} \tag{3}$$

where **I** denotes the unit matrix. We now again follow Baxter[9] and do a Wiener-Hopf type splitting using an auxilliary function $\hat{\mathbf{q}}$ and its adjoint $\mathbf{q}^+$ as follows

$$\mathbf{I} - \tilde{\mathbf{c}}(k) = [\mathbf{I} - \tilde{\mathbf{q}}^+(-k)][\mathbf{I} - \tilde{\mathbf{q}}(k)]. \tag{4}$$

Eqs. (4) and (3) now yield

$$\tilde{\mathbf{c}}(k) = \tilde{\mathbf{q}}(k) + \tilde{\mathbf{q}}^+(-k) - \tilde{\mathbf{q}}^+(-k)\tilde{\mathbf{q}}(k) \tag{5}$$

and

$$\tilde{\mathbf{h}}(k) - \tilde{\mathbf{q}}(k) - \tilde{\mathbf{q}}(k)\tilde{\mathbf{h}}(k) = \tilde{\mathbf{f}}(k) \tag{6}$$

where the function $\tilde{\mathbf{f}}$ satisfies

$$\tilde{\mathbf{f}}(k) - \tilde{\mathbf{f}}(k)\tilde{\mathbf{q}}^{+}(-k) - \tilde{\mathbf{q}}^{+}(-k) = 0. \tag{7}$$

We may now invert Eqs. (5), (6) and (7) in terms of one dimensional Fourier transform i.e.,

$$F_{\alpha\beta}(r) = \frac{1}{\sqrt{\rho_\alpha \rho_\beta}} \int_{-\infty}^{\infty} e^{-ikr} [\tilde{\mathbf{f}}]_{\alpha\beta}\, dk. \tag{8}$$

If we further constrain the function $Q_{\alpha\beta}(r)$ such that

$$Q_{\alpha\beta}(r) = 0 \qquad \text{if} \qquad r < (R_\alpha - R_\beta)|2 = D_{\alpha\beta} \tag{9}$$

and

$$Q_{\alpha\beta}(r) = 0 \qquad \text{if} \qquad r > (R_\alpha + R_\beta)|2 = S_{\alpha\beta} \tag{10}$$

then we obtain

$$C_{\alpha\beta}(r) = Q_{\alpha\beta}(r) - \sum_{\gamma} \rho_\gamma \int_{D_{\gamma\alpha}}^{U} Q_{\gamma\alpha}(t)\, Q_{\gamma\beta}(r + t)\,dt \tag{11}$$

and

$$H_{\alpha\beta}(r) = Q_{\alpha\beta}(r) - \sum_{\gamma} \rho_\gamma \int_{D_{\alpha\gamma}}^{S_{\alpha\gamma}} Q_{\alpha\gamma}(t)\, H_{\gamma\beta}(|r - t|)\,dt \tag{12}$$

where

$$U = \min[S_{\gamma\alpha}; S_{\gamma\beta} - r].$$

It follows from Eqs. (7), (8) and (9) that

$$F_{\alpha\beta}(r) = 0 \qquad \text{if} \qquad r > D_{\alpha\beta} \tag{13}$$

and furthermore from Eq. (11) that

$$C_{\alpha\beta}(r) = 0 \qquad \text{if} \qquad r > S_{\alpha\beta}$$

We note here that Eqs. (2) and (8) imply that

$$\left.\begin{matrix} C_{\alpha\beta}(r) \\ H_{\alpha\beta}(r) \end{matrix}\right\} = 2\pi \int_{r}^{\infty} \left\{\begin{matrix} c_{\alpha\beta}(r) \\ h_{\alpha\beta}(r) \end{matrix}\right\} r\,dr. \tag{15}$$

We may now differentiate Eqs. (11) and (12) using Eq. (15) to obtain

$$-2\pi r c_{\alpha\beta}(r) = Q'_{\alpha\beta}(r) - \sum_{\gamma} \rho_\gamma \int_{D_{\gamma\alpha}}^{U} Q_{\gamma\alpha}(t)\, Q'_{\gamma\beta}(r + t)\,dt \tag{16}$$

and

$$-2\pi r h_{\alpha\beta}(r) = Q'_{\alpha\beta}(r) - 2\pi\sum_{\gamma}\rho_{\gamma}\int_{D_{\alpha\gamma}}^{S_{\alpha\gamma}} Q_{\alpha\gamma}(t)(r - t)h_{\gamma\beta}(|r - t|)dt. \qquad (17)$$

Eqs. (16) and (17) constitute the required splitting of the Ornstein-Zernike relation. They must now be supplemented by a closure relation such as is provided by the Percus-Yevick or hyper netted chain approximations and in general it is necessary to resort to numerical methods. However if the attractive component of the interparticle potential is short ranged then we may obtain an analytic expression for $Q_{\alpha\beta}(r)$ from Eq. (17).

We note that virial expansions for strong short range potentials suggest

$$h_{\alpha\beta}(r) \sim -1 + \frac{\lambda_{\alpha\beta}}{12} S_{\alpha\beta}\delta(r - S_{\alpha\beta}) \quad D_{\alpha\beta} \ll r \ll S_{\alpha\beta} \qquad (18)$$

where the first term on the RHS of Eq. (18) arises from the hard core part of the potential and the second term, arising from the attractive component, is proportional to a dimensionless parameter, $\lambda_{\alpha\beta}$. Now if in Eq. (17) we restrict ourselves to the region $D_{\alpha\beta} < r < S_{\alpha\beta}$ and $D_{\alpha\gamma} \ll t \ll S_{\alpha\gamma}$ we have $r - t < S_{\beta\gamma}$ and $t - r < S_{\beta\gamma}$. We may therefore replace $h_{\alpha\beta}$ by -1 to obtain

$$Q'_{\alpha\beta}(r) = A_{\alpha} r + B_{\alpha} \qquad D_{\alpha\beta} < r < S_{\alpha\beta} \qquad (19)$$

where

$$A_{\alpha} = 2\pi\left[1 - \sum_{\gamma}\rho\gamma\int_{D_{\alpha\gamma}}^{S_{\alpha\gamma}} Q_{\alpha\gamma}(t)dt\right] \qquad (20)$$

and

$$B_{\alpha} = 2\pi\sum_{\gamma}\rho_{\gamma}\int_{D_{\alpha\gamma}}^{S_{\alpha\gamma}} t\, Q_{\alpha\gamma}(t)dt. \qquad (21)$$

Integrating Eq. (19) now gives

$$Q_{\alpha\beta}(r) = \frac{A_{\alpha}}{2}(r^2 - S_{\alpha\beta}^2) + B_{\alpha}(r - S_{\alpha\beta}) + \frac{\lambda\alpha\beta}{12} S_{\alpha\beta}^2 D_{\alpha\beta} < r < S_{\alpha\beta}. \qquad (22)$$

We note here that for a continuous potential function the functions $c_{\alpha\beta}$, $h_{\alpha\beta}$ and $Q_{\alpha\beta}$ are continuous. However for our model pseudo potential, the function $Q_{\alpha\beta}$ is discontinuous at $r = S_{\alpha\beta}$.

We determine the parameters $\{\lambda_{\alpha\beta}\}$ by introducing the P–Y closure relation which may be expressed as follows

$$1 + h_{\alpha\beta}(r) = [1 + f_{\alpha\beta}(r)]P_{\alpha\beta}(r) \qquad (23)$$

where

$$1 + f_{\alpha\beta}(r) = e^{-\beta\phi_{\alpha\beta}(r)} \tag{24}$$

$$P_{\alpha\beta}(r) = 1 + h_{\alpha\beta}(r) - C_{\alpha\beta}(r) \tag{25}$$

and $\phi_{\alpha\beta}(r)$ is the interparticle potential.

The interparticle potential chosen by Baxter for the one component system may be readily generalised to a multicomponent system and we obtain

$$e^{-\rho\phi_{\alpha\beta}(r)} = \begin{cases} \dfrac{S_{\alpha\beta}}{12\tau_{\alpha\beta}}\,\delta(r - S_{\alpha\beta}) & r \ll S_{\alpha\beta}. \\ 1 & S_{\alpha\beta} < r \end{cases} \tag{26}$$

The potentials $\{\phi_{\alpha\beta}(r)\}$ are thus characterised by the parameters $\{\tau_{\alpha\beta}\}$. Now from Eqs. (18), (23) and (26) we readily obtain

$$P_{\alpha\beta}(S_{\alpha\beta}) = \lambda_{\alpha\beta}\tau_{\alpha\beta}. \tag{27}$$

We may now obtain another expression for $P_{\alpha\beta}(S_{\alpha\beta})$. Thus from Eqs. (16) and (17) we have

$$\begin{aligned} 2\pi r\,P_{\alpha\beta}(r) = 2\pi r &- \sum_{\gamma} \rho_\gamma \int_{D_{\gamma\alpha}}^{U} Q_{\alpha\gamma}(t)\,Q'_{\gamma\beta}(r + t)\,dt \\ &+ 2\pi \sum \rho_\gamma \int_{D_{\alpha\gamma}}^{S_{\alpha\gamma}} Q_{\alpha\gamma}(t)(r - t)\,h_{\gamma\beta}(|r - t|)\,dt. \end{aligned} \tag{28}$$

If $r \to S_{\alpha\beta}$ from below then we may substitute Eq. (18) into (28). Noting also that $U \to D_{\gamma\alpha}$ and that the second term on the RHS vanishes we have

$$\begin{aligned} P_{\alpha\beta}(S_{\alpha\beta}) &= A_\alpha + \frac{B_\alpha}{S_{\alpha\beta}} + \\ &\frac{1}{S_{\alpha\beta}} \sum \rho_\gamma \int_{D_{\alpha\gamma}}^{S_{\alpha\gamma}} Q_{\alpha\gamma}(t)(S_{\alpha\beta} - t)\,\frac{\lambda_{\gamma\beta} S_{\gamma\beta}}{12}\,\delta(|S_{\alpha\beta} - t| - S_{\gamma\beta})\,dt. \end{aligned} \tag{29}$$

Now if $D_{\alpha\gamma} \ll t \ll S_{\alpha\gamma}$ then $S_{\alpha\beta} - t \ll S_{\beta\gamma}$ and the integral over the delta function yields a contribution, i.e.,

$$P_{\alpha\beta}(S_{\alpha\beta}) = A_\alpha + \frac{B_\alpha}{S_{\alpha\beta}} + \sum_{j} \rho_\gamma \frac{\lambda_{\gamma\beta} S^2_{\gamma\beta}}{12 S_{\alpha\beta}} Q_{\alpha\gamma}(D_{\alpha\gamma}). \tag{30}$$

Combining Eqs. (27) and (30) yields a set of coupled quadratic equations for the parameters $\{\lambda_{\alpha\beta}\}$. Thus

$$\lambda_{\alpha\beta}\tau_{\alpha\beta} = A_\alpha + \frac{B_\alpha}{S_{\alpha\beta}}\sum_\gamma \rho_\gamma \frac{\lambda_{\alpha\beta}S^2_{\alpha\beta}}{12S_{\alpha\beta}}Q_{\alpha\gamma}(D_{\alpha\gamma}). \tag{31}$$

These equations must be solved in conjunction with Eqs. (20)–(22).

2 BULK PROPERTIES OF THE ONE COMPONENT FLUID

The bulk properties have been investigated by Baxter. In this section we present results necessary to proceed with the adsorption problem and review the general features of the bulk properties. From Eqs. (20)–(22) it follows after some algebra that for the one component system

$$A_l = \frac{-\lambda_{ll}\eta}{1-\eta} + 2\pi\frac{(1+2\eta)}{(1-\eta)^2} \tag{32}$$

$$\frac{B_l}{S_{ll}} = \frac{\lambda_{ll}\eta}{2(1-\eta)} - \frac{3\pi\eta}{(1-\eta)^2} \tag{33}$$

and

$$\rho_l Q_{ll}(0) = \frac{6\eta}{\pi S_{ll}}\left[\frac{\lambda_{ll}}{12} - \frac{\pi}{1-\eta}\right] \tag{34}$$

where we have introduced the reduced density $\eta = \pi\rho_l S^3_{ll}/6$.

Furthermore from Eq. (31) we have

$$\lambda_{ll}\tau_{ll} = A_l + \frac{B_l}{S_{ll}} + \frac{\lambda_{ll}S_{ll}}{12}\rho_l Q_{ll}(0). \tag{35}$$

Substituting Eqs. (32)–(34) into (35) gives a quadratic equation for $\lambda = \lambda_{ll}/2\pi$

$$\frac{\eta\lambda^2}{12} - \left(\frac{\eta}{1-\eta} + \tau\right)\lambda + \frac{1+\eta/2}{(1-\eta)^2} = 0. \tag{36}$$

If $\tau > \tau_c = (2-\sqrt{2})/6 \simeq 0.0976$ there are two real positive solutions to Eq. (36) throughout the density range $0 < \eta < 1$. Below this value there exists a range of densities for which no real solutions exist so the system must undergo a discontinuous transition between states of different density. In other words, the model exhibits a first order phase transition. With critical "temperature" τ_c and associated critical density $\eta_c = (3\sqrt{2}-4)/2 \simeq 0.1213$. Note that this density is well below the close packing density $\eta = \pi/3\sqrt{2} \simeq 0.74$. When two real solutions for λ exist it is necessary to reject the larger solution since it must be continuous and take the zero density value $1/\tau$ (cf. Eq. (35)). Baxter also pointed out that a further criterion must be satisfied, namely that the integral $\int \mathrm{d}\mathbf{r}h(|\mathbf{r}|)$ be absolutely convergent. This implies that

$$\lambda\eta(1-\eta)=\mu<1+2\eta. \tag{37}$$

In figure 1 we have plotted the physical solution to Eq. (36)

$$\lambda=\frac{6}{\eta}\left(\frac{\eta}{1-\eta}+\tau\right)-\sqrt{\frac{36}{\eta^2}\left(\frac{\eta}{1-\eta}+\tau\right)^2-\frac{6(2+\eta)}{\eta(1-\eta)^2}} \tag{38}$$

and indicated the physical sub region bounded by curves A and B.

The thermodynamic properties may be obtained by using any one of a number of different relations. If we had solved exactly for the statistics mechanics of our particles rather than using the P-Y approximation, the different methods would all be equivalent. Unfortunately this is not so and Baxter discusses two different results for the pressure. Specifically he shows that the result obtained via the virial theorem exhibits unphysical features; whereas the result obtained via the compressibility is very similar to that of a van der Waals gas. In the region where λ is continuous for all permissible values of the density Baxter obtains the following analytic expression for the compressibility pressure

$$\frac{P}{\rho_l kT}=\frac{1+\eta+\eta^2-\mu(1+\eta/2)+\mu^3/36\eta}{(1-\eta)^3}. \tag{39}$$

Below the critical point expression (39) may be continued analytically into the condensed phase and so give the pressure in either phase.

4 ADSORPTION

We shall now follow in the footsteps of our earlier work[1] and restrict ourselves to a system consisting of only two types of particle. Species 1 constitutes the adsorbate and species 2 comprises only one particle which we shall later assume has an infinite radius so that it plays the role of an absorbent. As before we may define the adsorption excess, Γ, for our system as follows

$$\frac{\Gamma}{\rho_l}=\underset{R_2\to\infty}{\mathrm{Lt}}\;4\pi\int_{S_{12}^-}^{\infty}r^2h_{12}(r)\,\mathrm{d}r/4\pi S_{12}^2. \tag{40}$$

Integrating this expression by parts and using Eq. (15) gives

$$\frac{\Gamma}{\rho_l}=\underset{R_2\to\infty}{\mathrm{Lt}}\left\{\frac{H_{12}(S_{12}^-)}{2\pi S_{12}}+\frac{\int_{S_{12}^-}^{\infty}H_{12}(r)\,\mathrm{d}r}{2\pi S_{12}^2}.\right\} \tag{41}$$

Now we recall Eq. (12) which for our system may be written as

$$H_{12}(r) = Q_{12}(r) + \rho_l \int_0^{S_l} Q_{ll}(t)\, H_{12}(|r - t|)dt \tag{42}$$

and note from Eqs. (15) and (18) that

$$H_{12}(r) = -\pi(S_{12}^2 - r^2) + H_{12}(S_{12}^-) \quad r < S_{12}. \tag{43}$$

From Eqs. (41)–(43) it now follows that

$$\frac{\Gamma}{\rho_l} = \underset{R_2 \to \infty}{\mathrm{Lt}} \left\{ \frac{Q_{12}(S_{12}^-)/2\pi S_{12}}{1 - \rho_l \int_0^{S_l} Q_{ll}(t)dt} \right\} - \frac{\rho_l \int_0^{S} Q_{ll}(t)t\, dt}{1 - \rho_l \int_0^{S} Q_{ll}(t)dt}. \tag{44}$$

The derivation is identical to that given in our previous work[1] (although we note here that in reference 1 $Q_{\alpha\beta}$ was defined with a minus sign) and we refer the reader there for further details. We may substitute for the functions $Q_{\alpha\beta}$ in Eq. (44) using Eqs. (20)–(22) to obtain

$$\frac{\Gamma}{\rho_l} = \underset{R_2 \to \infty}{\mathrm{Lt}} \left\{ \frac{\lambda_{12} S_{12}}{12 A_1} \right\} - \frac{B_1}{A_1}. \tag{45}$$

Now from Eq. (31) we immediately obtain

$$\lambda_{12} = \frac{A_1 + B_1/S_{12}}{\tau_{12} - \frac{\rho_l S_{12}}{12}} Q_{ll}(0). \tag{46}$$

If we now introduce the notation $\Phi_{12} = S_{12}/12\tau_{12}$ we obtain from Eqs. (45) and (46) after taking the limit $R_2 \to \infty$, the expression

$$\frac{\Gamma}{\rho_l} = \frac{\Phi_{12}}{1 - \rho_l \Phi_{12} Q_{ll}(0)} - \frac{B_1}{A_1}. \tag{47}$$

We now see that apart from the parameter Φ_{12}, which from its definition is clearly a measure of the strength of the adsorbate/adsorbent potential, the adsorption excess has been expressed entirely in terms of the bulk properties of the adsorbate. Thus we may use expressions (32)–(34) to obtain finally the adsorption excess as a function of reduced density:

$$\Gamma(\eta) = \frac{6}{\pi S_1^2} \left\{ \frac{\alpha\eta}{1 - \alpha\eta\left(\lambda - \frac{6}{1 - \eta}\right)} + \frac{\eta^2}{2}\left(\frac{3 - 2(1 - \eta)}{1 + 2\eta - \lambda\eta(1 - \eta)}\right) \right\} \tag{48}$$

where $\alpha = \Phi_{12}/S_1$ and we recall that $\lambda = \lambda(\eta)$ is given by Eq. (38).

Before doing detailed numerical calculations, a number of interesting features of this expression deserve immediate comment.

In the limit of very low gas density $\eta \ll 1$, weak adsorbate/adsorbent interactions $\alpha\eta \ll 1$, and weak adsorbate/adsorbate interactions $\lambda \sim {}^1/\tau < 6$ then the second term on the RHS of Eq. (48) may be neglected since it is $0(\eta^2)$ and the first term reduces to give

$$\Gamma(\eta) \simeq 6\alpha\eta/\pi S_1^2 + 0(\eta^2) \tag{49}$$

which is the well known Henry limiting law.

If we relax the condition that the adsorbate/adsorbent interaction be weak and admit conditions such that $\alpha\eta \gg 1$ then again the second term on the RHS of Eq. (48) may be neglected and the first term reduces to give

$$\Gamma(\eta) \simeq {}^1/\pi S_1^2 - 0({}^1/\alpha\eta;\, \eta^2) \tag{50}$$

Thus for weak adsorbate/adsorbate interactions but strong adsorbate/adsorbent interactions, the adsorption isotherm exhibits a saturation region corresponding roughly to close packing on the adsorbent of a monolayer of gas molecules.

If both adsorbate/adsorbate and adsorbate/adsorbent interactions are weak then Eq. (48) reduces to an equation obtained elsewhere (Eq. 42 in reference 1) which over the density range $0 \ll \eta < 1$ was shown to yield adsorption isotherms typical of gases at high temperatures and pressures.

By far the most significant is that depending on the values of the interaction parameters α and τ, the isotherm can exhibit multi-layer wetting. To see this we note first that the denominator of the second term can never be zero in the physical region (cf. Eq. (37)). However for τ sufficiently small such that $\lambda(\eta) - \dfrac{6}{1-\eta} > 0$ and α sufficiently large then the denominator of the first term in Eq. (48) can become zero. Thus the adsorption excess diverges which is typical of multi-layer wetting. We emphasise that to obtain multi-layer wetting, it is not sufficient to have strong adsorbate/adsorbent interactions; the adsorbate/adsorbate interaction must also be strong too. This may be achieved by lowering the temperature. In Fig. 1 we have plotted the line $\lambda = \dfrac{6}{1-\eta}$ which delineates the non-wetting and multi-layer wetting regions. Now if the adsorbate/adsorbate interaction is sufficiently large for multi-layer wetting to occur and the adsorbate/adsorbent interaction is very large such that the denominator of the first term in Eq. (48) diverges for small values of the reduced density, η, then we may to leading order neglect the second term on the RHS and also replace λ by its value at zero density (see Fig. 1) to obtain,

$$\Gamma(\eta) \approx \frac{6}{\pi S_1^2}\left[\frac{\alpha\eta}{1 - \alpha\eta({}^1/\tau - 6)}\right] \tag{51}$$

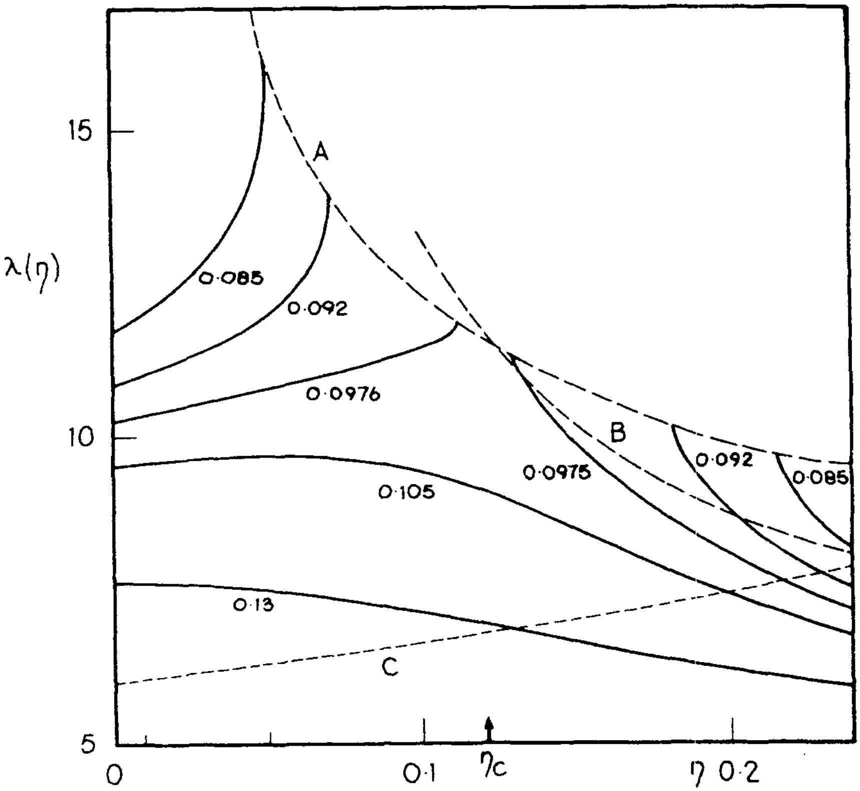

FIGURE 1 A plot of the physical component of the function λ given by Eq. (38) for various values of the interaction parameter τ. Curve A marks the boundary between the physical and non-physical branches. All points above curve B correspond to solutions for which the radial distribution function for the one component system is divergent.

Curve C separates the wetting and non-wetting regions in the sense that for a point below the curve multi-layer wetting may not occur no matter how large the adsorbate/adsorbent interaction is.

Three different types of gas adsorption isotherms are obtained from such a function. Two correspond to types I $\left(\frac{1}{\tau} < 6\right)$ and III $\left(\frac{1}{\tau} > 6\right)$ in the usual BET classification. (The third occurs when $\tau = 1/6$ and is not covered in the BET classification.) However note that as $\eta \to 1$, Γ will always tend to $^3/\pi S_1^2$. This is because the first term on the RHS of Eq. (48) ultimately tends to zero and the second term dominates.

We have examined the complete expression for various values of the parameters and the results are shown in the remaining figures. In Figure 2 the parameter α is unity. For low densities $\eta \lesssim 0.05$ they are linear. For larger η the isotherms level out and then decrease with increasing η. For $\tau = 0.13$,

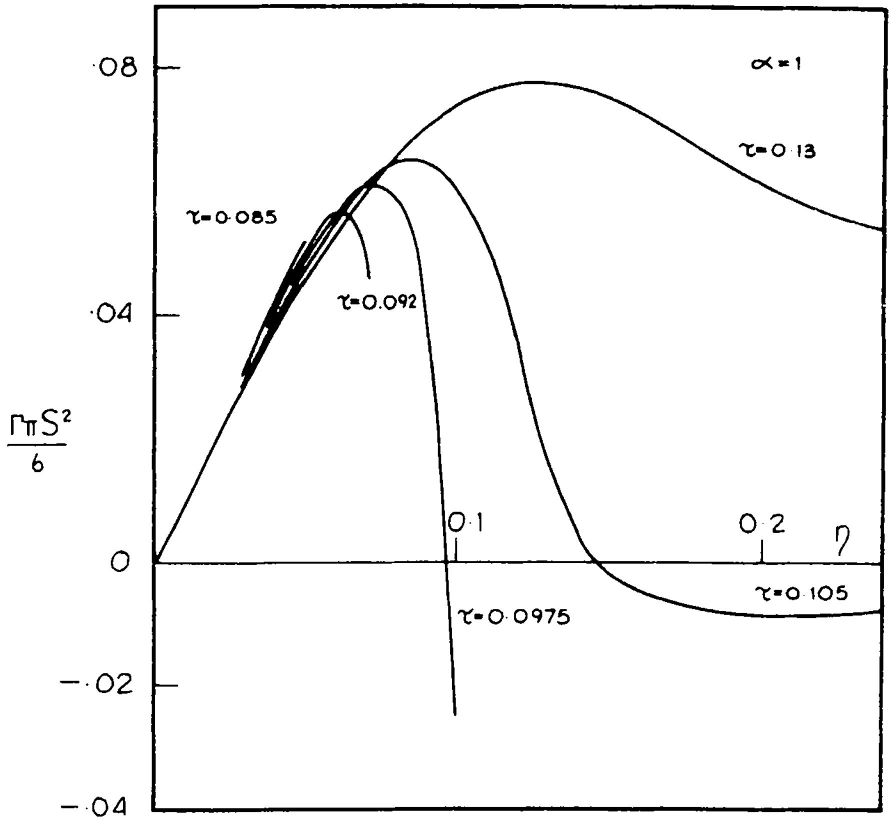

FIGURE 2 The reduced adsorption excess $\Gamma\pi S_1^2/6$ for $\alpha = 1$ given by Eq. (48). The curves for $\tau \leq 0.0975$ end at the limit of the physical region.

the behaviour is typical of high pressure gas adsorption. For lower temperatures and/or weaker adsorbate/adsorbate interactions, the adsorption excess decreases more rapidly and may become negative. This negative result arises from the second term on the RHS of Eq. (48) which increases in importance as $\eta \rightarrow 1$. (This is illustrated graphically in Figure 3 which shows the contribution to the adsorption excess from the first term only in Eq. (48).) For values of $\tau < \tau_c \simeq 0.0976$ the adsorption excess is inly defined in the physical region and for $\alpha = 1$ multi-layer wetting does not occur. In Figure 4 the same isotherms are plotted for $\alpha = 2$. In this case for $\tau > \tau_c$ the isotherms do not become negative; the second term on the RHS of Eq. (48) although significant does not now dominate. For $\tau < \tau_c$ the isotherms diverge inside the physical region defined according to Figure 1. However in typical gas adsorption experiments the reduced densities are much smaller than 0.1 and yet multi-layer wetting still occurs. We may simulate this situation by

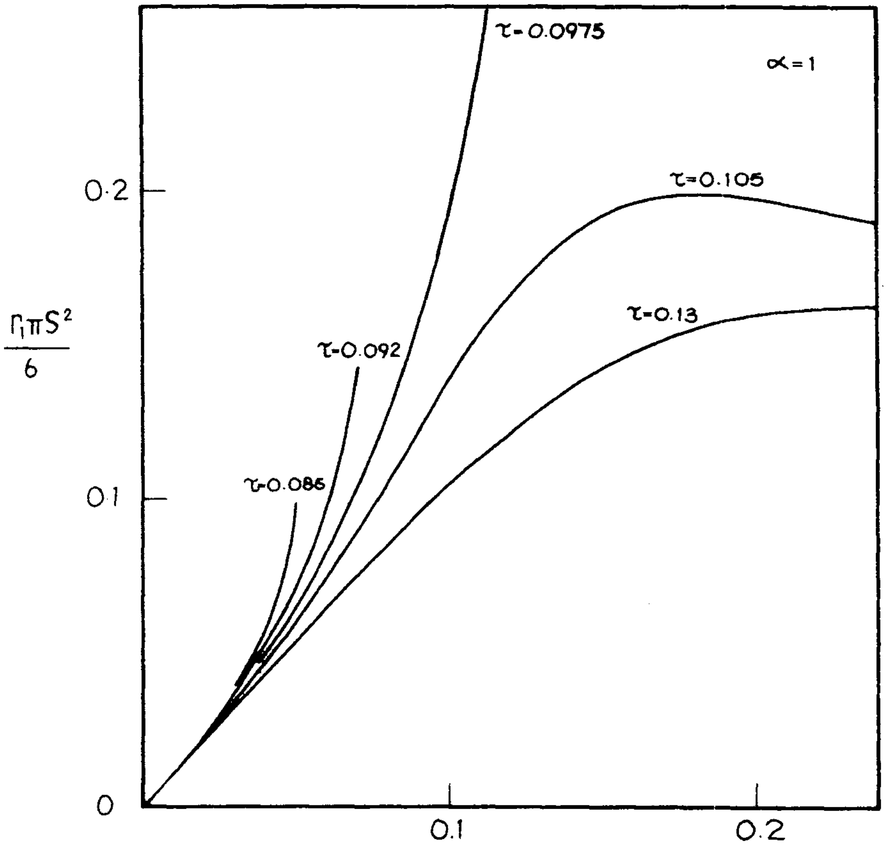

FIGURE 3 The component of the reduced adsorption excess for $\alpha = 1$ given by the first term only on the RHS of Eq. (48).

increasing α. Figure 5 shows the adsorption isotherms for $\alpha = 30$, a not unreasonable value (see Eq. 53). These isotherms correspond to those referred to earlier which occur for large values of α.

5 DISCUSSION

In this paper we have shown how using a model which includes molecular correlations in a non trivial way a theory of mono-layer and multi-layer wetting can be obtained according to the values of the various parameters. Specifically we find that multi-layer wetting is not obtained unless the

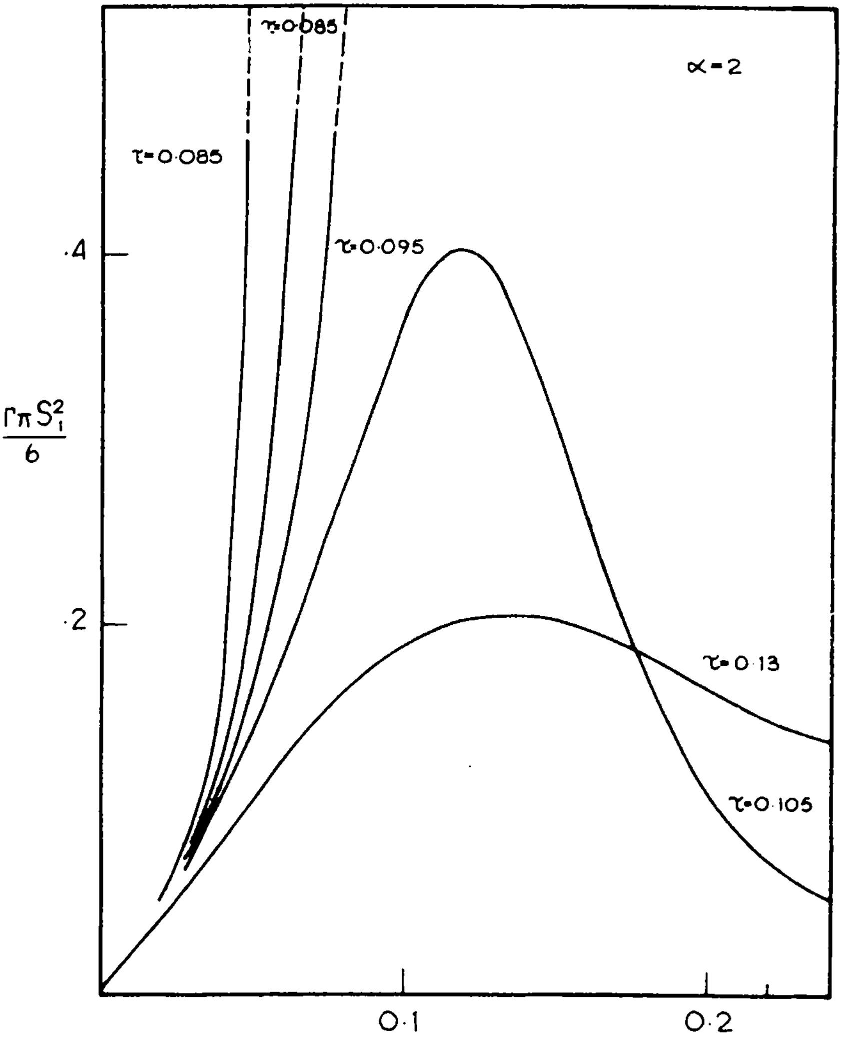

FIGURE 4 The reduced adsorption excess $\Gamma\pi S_1^2/6$ for $\alpha = 2$ given by Eq. (48). The curves for $\tau \leq 0.0975$ are dotted to indicate they ultimately diverge within the physical region defined in Figure 1.

adsorbate/adsorbate interaction is sufficiently strong (i.e. τ sufficiently small). This is irrespective of the strength of the adsorbate/adsorbent interaction, α. Of course, when τ is small enough, larger values of α will ensure that multi-layer wetting occurs at lower densities.

In order to compare our results more directly with real systems one might

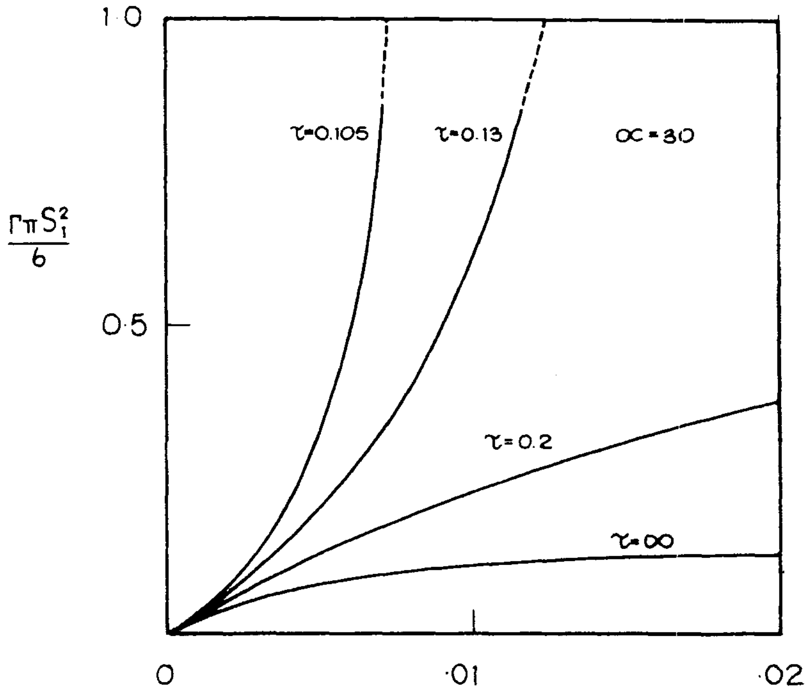

FIGURE 5 The reduced adsorption excess $\Gamma\pi S_1^2/6$ for $\alpha = 30$ given by Eq. (51). The curves for $\tau = 0.13$ and $\tau = 0.105$ are dotted to indicate they diverge indicating multi-layer wetting is occurring. For large values of τ, the isotherms exhibit saturation characteristic of BET type I isotherms.

define the parameters τ and α via second virial coefficients. Thus,

$$\frac{S_1}{12\tau} = \frac{1}{S_1^2}\int dr\, r^2 (e^{-\beta\phi_{11}(r)} - 1) \tag{52}$$

and

$$\phi_{12} = \int dz\, (e^{-\beta\phi_{12}(r)} - 1). \tag{53}$$

However whilst such an identification might give qualitative agreement, this does not overcome the limitation noted above that in the limit of low pressure adsorption only two types of isotherm are obtained. It is likely that a solution which incorporates the inter-particle potential $\phi_{\alpha\beta}(r)$ explicitly will overcome this limitation and give a wider variety of isotherms depending on the range of the potentials. However in general no analytic solution is possible and the solutions must be obtained numerically.

Apart from the extension suggested above, this work may be readily generalised to adsorption of more than one species. Indeed the model forms a firm base from which a comprehensive study of adsorption can be made. One can also use the models to consider the effect of adsorption on the interaction of two adsorbing surfaces. The solution to this problem will complement recent thermodynamic studies of this particular problem.[10,11] These generalisations are currently being studied.

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