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# Physical Adsorption and the Free Volume Model for Liquids

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**S**URFACE tension has been treated by Lennard-Jones and Corner,<sup>1</sup> using a free volume model for the liquid state. We extend this method here to a liquid-like adsorbate (of, say, three or more layers) on a free adsorbent surface.

For a "free-volume" liquid,<sup>2</sup>

$$-A_0/kT = N[\ln(2\pi mkT/h^2)^{3/2}(T) + 1 + \ln v_f^0 + (\chi_0/kT)]. \quad (1)$$

Consider a molecule at  $x, y, z$  in a cell with center at  $x', y', z'$  (same origin). If we now remove the liquid occupying the regions  $z < 0$  and  $z > h$  and insert the adsorbent in the region  $z < 0$ , we have a slab of adsorbate (assumed as a first approximation to have the liquid density uniformly) between  $z = 0$  and  $z = h$ . This alters the potential field in which the molecule is moving from  $\varphi_0$  to

$$\varphi = \varphi_0 - \Phi(z) - \Phi(h-z) + \varphi_a(z), \quad (2)$$

where  $\Phi(z)$  is the energy of interaction of a molecule at  $z$  with the semi-infinite liquid,  $z < 0$ , and  $\varphi_a(z)$  is analogous for the adsorbent,  $z < 0$ . Suppose the minimum in  $\varphi$  is at  $z = z_0$ . Then for the adsorbate, we replace  $N$ ,  $-\chi_0$ , and  $v_f^0$  in Eq. (1) by  $Ndz'/h$ ,

$$-\chi(z') = \frac{1}{2}\varphi_0(z_0 - z') - \frac{1}{2}\Phi(z_0) - \frac{1}{2}\Phi(h - z_0) + \varphi_a(z_0), \quad (3)$$

and

$$v_f(z') = \int \exp[-(\varphi - \varphi(z_0))/kT] dx dy dz, \quad (4)$$

and integrate<sup>3</sup> from  $z' = 0$  to  $z' = h$  to give  $-A/kT$ . Then,

$$\ln p/p_0 = \partial[(A - A_0)/kT]/\partial N \quad (5)$$

$$(A - A_0)/kT = N[\ln v_f^0 - \langle \ln v_f \rangle_{Av} + (\chi_0 - \bar{\chi})/kT], \quad (6)$$

where  $\bar{\chi}$  is  $\chi(z')$  averaged from  $z' = 0$  to  $z' = h$ , etc.

As an initial rough approximation, we cancel<sup>4</sup> the free volume terms in Eq. (6) (putting  $z_0 = z'$ ) and compute  $\chi_0 - \bar{\chi}$

from a van der Waals model<sup>4</sup> (neighbor distribution *uniform* outside of  $r = r^*$ ), taking for the interaction between two liquid molecules,

$$u(r) = \infty \quad r \leq r^* \\ = -\epsilon(r^*/r)^6 \quad r > r^*. \quad (7)$$

An analogous expression (parameters  $\epsilon_1, r_1$ ) is used for the liquid molecule-adsorbent molecule interaction. From<sup>5</sup> Eqs. (5) and (6), without further approximation, we find eventually (details to be published)

$$\ln p/p_0 = (\delta/\Gamma^3) - [\delta_1/(\Gamma + r_1\rho)^3] \quad (8)$$

$$\cong (\delta - \delta_1)/\Gamma^3 \quad (9)$$

$$\delta = \pi\rho^4\epsilon r^{*6}/6kT \quad (10)$$

$$\delta_1 = \pi\rho_1\rho^3\epsilon_1 r_1^6/6kT, \quad (11)$$

where  $\Gamma = N/\mathcal{A}$ ,  $\rho$  is the liquid density ( $N/V$ ),  $\rho_1$  the adsorbent density, and  $\mathcal{A}$  the surface area. The case of physical interest is  $\delta - \delta_1 < 0$ . The power three in Eq. (9) follows from Eq. (7) (i.e.,  $m = 3$  with  $m = 6$ ). Introduction of a repulsive term should, *in effect* (for  $h$  not too large), reduce this power slightly. Near  $p/p_0 = 1$ ,  $\Gamma$  is proportional to  $[1 - (p/p_0)]^{-1}$ . This leads to convergence at  $p/p_0 = 1$  of the Gibbs integral for the surface pressure.

Halsey<sup>6</sup> has obtained essentially Eq. (9) by a rather less explicit argument. He finds excellent agreement with experiment for  $N_2$  on anatase with 2.267 in place of 3 in Eq. (9).

We are using a modified Lennard-Jones and Devonshire liquid model for a detailed application of Eqs. (2)–(6).

In a future note we shall outline the analogous extension of Fowler's<sup>1,7</sup> treatment of surface tension.

<sup>1</sup> Lennard-Jones and J. Corner, *Trans. Faraday Soc.* **36**, 1156 (1940); J. Corner, *ibid.* **44**, 1036 (1948). Also, see J. G. Kirkwood and F. P. Buff, *J. Chem. Phys.* **17**, 338 (1949), for a rigorous treatment.

<sup>2</sup> T. L. Hill, *J. Phys. and Coll. Chem.* **51**, 1219 (1947).

<sup>3</sup> In calculations it will probably prove desirable to treat the top and bottom layers separately, as in reference 1 (top layer). Otherwise, a smeared out (average) distribution of cell centers is physically realistic.

<sup>4</sup> T. L. Hill, *J. Chem. Ed.* **25**, 347 (1948).

<sup>5</sup> Using Eq. (2) of T. L. Hill, *J. Chem. Phys.* **16**, 181 (1948).

<sup>6</sup> G. Halsey, *J. Chem. Phys.* **16**, 931 (1948).

<sup>7</sup> R. H. Fowler, *Proc. Roy. Soc. A* **159**, 229 (1937).