Effect of Attractive Forces on Monolayer Permeation and Evaporation Resistance

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The distribution of holes in a dense two-dimensional Lennard-Jones fluid appears similar to that in the equivalent hard disc fluid. Hence, in systems where a two-dimensional model reasonably represents the structure of a monolayer adsorbed at the gas–liquid interface, the permeation rate and evaporation resistance should be insensitive to the details of the attractive forces between the monolayer molecules.

It has been shown [1] that the resistance of a monolayer film to solvent evaporation may be related to the probability of finding holes in a two-dimensional model of the fluid surface. The model considered [1] was the hard disc fluid, and the hole probability $\mathscr{P}$ was determined by a molecular dynamics sampling technique. The intention of this Note is to show that neglecting attractive forces leads to negligible error at high surface densities; at low densities, however, the absence of " clustering " in the hard disc fluid implies a slight overestimate in the predicted evaporation resistance, particularly at low temperatures.

Attractive forces have two main effects: they change the two-dimensional fluid structure, and they perturb the trajectories of the permeating molecules. The effect on the trajectories is extremely complex, since it involves the influence of attractive forces in the bulk solvent on the rate of diffusion of the permeating molecules. On the other hand, such perturbations should have little effect on the predicted evaporation resistance if the force fields in the monolayer and bulk solvent are of similar strength; with this proviso it seems reasonable to limit discussion to the change in the two-dimensional structure.

Only for hard particles can a " hole " be strictly defined. In such a fluid, the potential energy Φ of interaction on the perimeter of an imaginary hole takes the values 0 or $+\infty$ depending upon whether it overlaps or not with at least one hard particle of diameter σ. The probability for hole formation of size $\bar{d}\sigma$ is then a canonical average of $e^{-\Phi}$ over all possible configurations of density ρ:

$$\mathscr{P}(\bar{d}, \rho) = \langle e^{-\Phi} \rangle. \tag{1}$$

In a soft core system, eqn (1) is generalized to a Boltzmann average,

$$\mathscr{P}(\bar{d}, \rho) = \langle \exp(-\Phi/kT) \rangle, \tag{2}$$

where T is the temperature. Widom has discussed [2] the relationship between this canonical average and the chemical potential μ:

$$\rho \exp(-\mu/kT) = \langle \exp(-\Phi/kT) \rangle. \tag{3}$$

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Here μ is the chemical potential at infinite dilution of an imaginary circular particle of diameter equal to that of the hole.

VAN DER WAALS FLUID

As an illustration of a simple system with attractive forces, let us consider a two-dimensional van der Waals mixture of two components. The pressure p is given by

$$p = RT/(A_m - b_m) - a_m/A_m^2, \qquad (4)$$

where A_m is the molar area, and a_m and b_m are (two-dimensional) van der Waals constants, given in the one-fluid approximation as a function of mole fraction x_1 of component 1 by the expressions:

$$a_m = x_1^2 a_{11} + 2x_1 x_2 a_{12} + x_2^2 a_{22}, \qquad (5)$$
$$b_m = x_1^2 b_{11} + 2x_1 x_2 b_{12} + x_2^2 b_{22}. \qquad (6)$$

The chemical potential of component 1 at infinite dilution is given by

$$\mu_1(T, A_m) - \mu_1^0(T, A_m^0) = -RT \ln [(A_m - b_{22})/A_m^0] +$$
$$RT(2b_{12} - b_{22})/(A_m - b_{22}) - 2a_{12}/A_m, \qquad (7)$$

where $\mu_1^0(T, A_m^0)$ is the infinite dilution chemical potential for an ideal gas of molar area A_m^0. In terms of hole probabilities,

$$\ln (\mathscr{P}/\mathscr{P}^0) = \ln [(A_m - b_{22})/A_m^0] + (2a_{12}/RTA_m)$$
$$- (2b_{12} - b_{22})/(A_m - b_{22}), \qquad (8)$$

where $\mathscr{P}^0$ is the ideal gas value. Given $\mathscr{P}^0$ as a function of density, the hole probability function, and hence the evaporation resistance, can be calculated directly. We note that $\mathscr{P}$ is independent of attractions between pairs of molecules in the monolayer (i.e., independent of a_{22}), and depends only on a_{12}, the attractive " hole-particle " interaction. In the high temperature limit the positive contribution to $\mathscr{P}$ from attractive forces gradually decreases to zero, and eqn (8) reduces to van der Waals's estimate of $\mathscr{P}$ for the hard disc fluid.

The van der Waals fluid contains molecules which interact with a pair potential of infinite range but zero depth.[3] While this representation often leads to a reasonable description of bulk macroscopic properties, there are good reasons to believe that it may be inadequate for estimating a quantity such as $\mathscr{P}$, which depends on the detailed microscopic structure. It seems appropriate, therefore, to consider a potential of more realistic range and softness, and the Lennard-Jones (12 : 6) potential is chosen for this purpose.

TWO-DIMENSIONAL LENNARD-JONES FLUID

An assembly of 144 Lennard-Jones (12 : 6) particles was simulated on a computer by the method of molecular dynamics, and hole probabilities calculated in a manner similar to that described previously.[1] The " predictor-corrector " simulation method of Rahman [4] was used, and temperature, pressure and pair distribution functions were calculated in situ. However, whereas the fluid structure itself was determined by solving equations of motion for particles interacting with a (12 : 6) potential, in estimating $\mathscr{P}$, an effective hard core interaction was assumed. The effective diameter was calculated from the theory of Weeks, Chandler and Andersen.[5] In this approach the potential is divided into reference and perturbation parts:

$$u_{\text{ref}}(r) = 4\varepsilon[(\sigma/r)^{12}-(\sigma/r)^6]+\varepsilon \quad (r < 2^{\frac{1}{6}}\sigma)$$
$$= 0 \quad (r \geqslant 2^{\frac{1}{6}}\sigma) \tag{9}$$
$$u_{\text{pert}}(r) = -\varepsilon \quad (r < 2^{\frac{1}{6}}\sigma)$$
$$= 4\varepsilon[(\sigma/r)^{12}-(\sigma/r)^6] \quad (r \geqslant 2^{\frac{1}{6}}\sigma).$$

Here ε and σ are the usual energy and size parameters and $(2^{\frac{1}{6}}\sigma)$ is the equilibrium separation distance. The effective hard core diameter d is estimated by minimizing to first order in ρ the difference between the soft and hard disc configuration integrals, i.e.,

$$\int_0^\infty y_0(r)\{\exp[-u_{\text{ref}}(r)/kT]-\exp[-u_0(r)/kT]\}r \, \mathrm{d}r = 0. \tag{10}$$

Steele has shown [6] that d may be expressed in the convenient form

$$d = d_{\text{BH}}+\sigma^*\delta/2, \tag{11}$$

where d_{BH} is the Barker–Henderson core diameter,[7]

$$d_{\text{BH}} = \int_0^\infty \{1-\exp[-u_{\text{ref}}(r)/kT]\} \, \mathrm{d}r. \tag{12}$$

The quantities d_{BH} and δ are independent of dimensionality and can be taken directly from the tabulation of Verlet and Weiss;[8] σ^* is calculated from the hard disc correlation function $y_0(r)$.

TABLE 1.—HOLE PROBABILITIES $\mathscr{P}(\bar{d}, \xi)$ FOR LENNARD-JONES (12 : 6) AND HARD DISC FLUIDS OF DENSITY $\xi = 0.64$

$\bar{d}$	$\ln \mathscr{P}(\bar{d}, \xi)$	
	hard discs	L–J discs
0	−1.02	−1.02
0.2	−1.99	−2.04
0.4	−3.42	−3.48
0.6	−5.39	−5.18

Table 1 shows hole probabilities $\mathscr{P}(\bar{d}, \xi)$ for an assembly of Lennard-Jones (12 : 6) particles at a density

$$\xi = \pi\rho d^2/4 \tag{13}$$

of 0.640 and a reduced temperature

$$\bar{T} = kT/\varepsilon \tag{14}$$

of 2.50. The probabilities are seen to approach very closely those for a fluid of hard discs of diameter $\sigma = d$, thus quantitatively confirming the previous supposition [1] that in the high density region $\mathscr{P}$ is determined overridingly by the repulsive interactions in the two-dimensional fluid. The density range over which this assumption is valid covers almost all the available experimental data for evaporation resistances of monolayer films.

In those cases where the monolayer density is low, however, the effect of molecular " clustering " may become significant. This is illustrated in fig. 1 which shows a representative " snapshot " of 144 Lennard-Jones (12 : 6) particles at $\xi = 0.407$ and $\bar{T} = 2.40$. We observe the presence of relatively large and long-lived holes which are absent in studies of hard discs and their mixtures.[1, 9] Fehder has found similar structural features [10] and has attributed the vacancies to a " microscopic surface

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tension " which causes particles preferentially to migrate along the edge of a vacancy rather than move out into unoccupied area (*sic*). Because of clustering effects, therefore, we might expect the hard disc model to be inapplicable below densities of, say, $\xi \sim 0.5$. This is about the same density below which effective circularity in the monolayer particles is likely to be a poor assumption,* and so it is probably necessary to allow for strong anisotropy in the pair interaction as well as an attractive contribution in this density region.
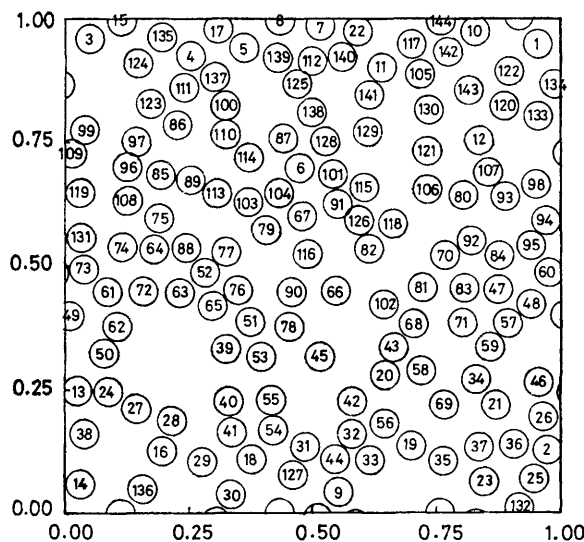

FIG. 1.—" Snapshot " of 144 Lennard-Jones (12 : 6) discs at density $\xi = 0.407$ and reduced temperature $\tilde{T} = 2.4$, $\rho = 0.520$, $\sigma = 0.060$. The particles are represented as circles of effective diameter given by eqn (9)-(12).

TABLE 2.—HOLE PROBABILITIES $\mathscr{P}(\bar{d}, \xi)$ FOR THE TWO-DIMENSIONAL LENNARD-JONES (12 : 6) FLUID OF DENSITY $\xi = 0.407$ AND REDUCED TEMPERATURE $\tilde{T}$

| | | $\ln \mathscr{P}(\bar{d}, \xi)$ | |
$\bar{d}$	$\tilde{T} = 0.98$	$\tilde{T} = 2.40$	$\tilde{T} = 16.1$
0.42	-1.2_7	-1.2_7	-1.1_9
0.83	-2.3_8	-2.3_6	-2.1_2
1.25	-3.5_1	-3.6_0	-3.4_5
1.67	-5.0_8	-4.9_8	-5.0_2

In addition to introducing attractive forces into the hard disc fluid, the Lennard-Jones interaction also incorporates a more realistic softness into the repulsive potential. In terms of the temperature dependence of $\mathscr{P}$, the two effects appear to work in opposite directions. Table 2 shows values of $\ln \mathscr{P}(\bar{d}, \xi)$ for reduced temperatures $\tilde{T} = 0.98$, $\tilde{T} = 2.40$ and $\tilde{T} = 16.1$ at a density $\xi = 0.407$, and within the estimated computational error (± 0.05), $\ln \mathscr{P}(\bar{d}, \xi)$ is essentially independent of temperature. There are two competing influences on the probability of hole formation : as $\tilde{T}$ is

* At low monolayer densities some of the chain molecules are believed to orientate themselves parallel to the surface, rather than being packed perpendicular to it as they are forced to be at high densities.

raised, " clustering " disappears and hence $\mathscr{P}$ decreases towards its effective hard disc value; at the same time, the faster particles approach more closely on collision, reducing the average surface area " covered " and thereby increasing $\mathscr{P}$.
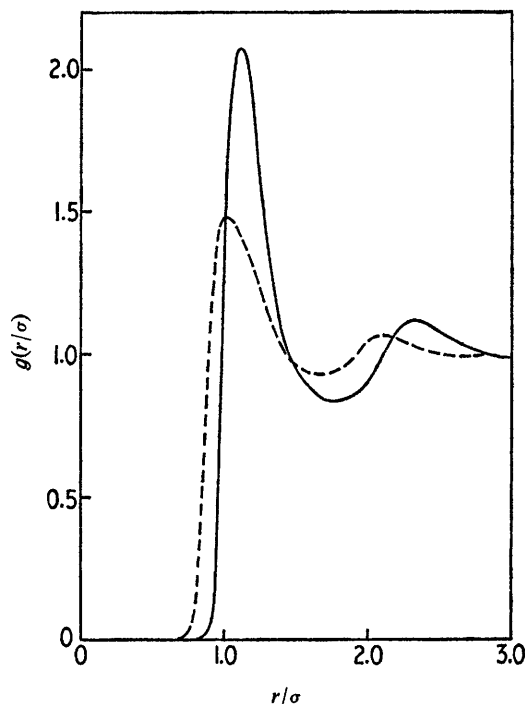

FIG. 2.—Pair distribution functions of a Lennard-Jones (12 : 6) fluid of density $\xi = 0.407$ as a function of the reduced separation (r/σ) : —, $\tilde{T} = 0.98$; – – –, $\tilde{T} = 16.1$.

The effect of temperature is seen most clearly by reference to the pair distribution function $g(r)$ (fig. 2). The peaks corresponding to $\tilde{T} = 16.1$ are both reduced in height and shifted to lower separations (r/σ) in comparison with those for $\tilde{T} = 0.98$. Thus, the closer molecular approach at high temperature would appear to approximately counterbalance the loss of clustering, with the overall effect of leaving $\mathscr{P}$, and hence the evaporation resistance, effectively unchanged.

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