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1981 J. Phys. A: Math. Gen. 14 L193

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LETTER TO THE EDITOR

Monte Carlo simulation of a model of a surfactant

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Received 17 February 1981

Abstract. A lattice gas model of a solution is described. Its Monte Carlo simulation shows surfactancy and strong evidence for a phase transition in the surface.

In this Letter a model of a dilute solution is studied which can show high concentrations of solute at the surface in equilibrium with a very dilute bulk solution. Such a system is said to display surfactancy. In the model described here this results, broadly speaking, from enhanced interactions between solute molecules when they lie in the surface. This enhancement could arise, for instance, because the surrounding medium has different dielectric properties from the solvent itself.

This raises the question whether enhanced surface interactions can alter the state of the surface of a solvent–solute system. It is known that increasing ferromagnetic bond strengths in the surface of a cubical Ising ferromagnet, or its lattice-gas equivalent, may induce the surface to undergo a phase transition to an ordered state at a temperature above the three-dimensional critical value (Binder and Hohenberg 1972, 1974). This result was obtained by series expansion techniques. There is also an exact result in this direction for the planar lattice (Abraham 1980). Below a two-component lattice-gas model will be developed along these lines.

Consider a two-component lattice gas in three dimensions. On a simple cubic lattice Λ with unit edge length let a variable $t(x) = 0, 1, 2$ be defined for each site x : $t(x) = 0$ denotes an empty cell centred on x , $t(x) = 1$ a cell occupied by a solvent molecule and $t(x) = 2$ a cell occupied by a solute molecule. Let a neighbouring pair of species i and j have an interaction energy u_{ij} and define $-\beta u_{ij} = E_{ij}$. Attractive interactions imply $E_{ij} \geq 0$. Let the molecular species $i = 1, 2$ have fugacities z_i and define H_i by $z_i = \exp H_i$. It is convenient to define projectors $P_j(x)$ onto species j at site x : evidently

$$P_1(x) = 2t(x)(1 - t(x)/2) \quad (1a)$$

and

$$P_2(x) = t(x)(t(x) - 1)/2. \quad (1b)$$

Let us regard the P_j as components of a two-vector P and introduce similar matrix notations for H_i and E_{ij} . The interaction energy of a configuration $\{t(x)\}$, multiplied by $-\beta$, is

$$E = \sum P(x)^T E P(y) \quad (2)$$

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where the sum is over nearest neighbour sites x and y , each pair being taken once. The grand canonical probability of $\{t(x)\}$ is

$$P(\{t\}; \Lambda, Z, E) = \Xi(\Lambda, Z, E)^{-1} \exp\left(\sum_x H^T P(x) + E\right) \quad (3)$$

where Ξ is the grand canonical partition function, which normalises (3). One may think of (3) as describing a generalised three-component Potts model. In solution language, the case $H_2 \rightarrow -\infty$ describes a solvent with critical parameters $H_1(c) = -2.66028$ and $E_{11}(c) = 0.88676$ taken from Ising-model data (Domb 1972).

Now consider a lattice Λ_s , the vertices x of which satisfy $x_3 \geq 0$; the lattice has a surface at $x_3 = 0$. Returning to (2), if $x_3 = y_3 = 0$, then the interaction matrix E is replaced by $E(S)$. Take $H_1 = 0$ and let $E_{22} < E_{11}$ be chosen so that the lattice is mainly occupied by solvent molecules. Suppose $E_{11}(S) = E_{11}$ and $E_{12}(S) = E_{12}$. Can $E_{22}(S)$ be chosen so that the surface layer is mainly occupied by solute molecules, even though such molecules are found infrequently in the bulk? Clearly the parameters in the problem can be selected so that such a state is stabilised energetically with respect to a ground state with all solvent molecules. For instance, take $E_{21}, E_{22} < E_{11}$ and $E_{22}(S) > E_{11}(S) + (E_{11} - E_{21})/2$. The question is then whether or not entropic considerations dominate energetic ones in determining the state of the surface and further, whether there is a phase transition for such a system in which the surface-segregated state becomes unstable.

Next we give numerical evidence from a Monte-Carlo simulation of a finite lattice Λ of size $10 \times 10 \times 16$ that as the ratio $\alpha = E_{22}(S)/E_{11}(S)$ increases from unity there is a sudden increase in the fractional population of solute in the surface, denoted $\rho_2(0)$, from essentially zero to slightly less than unity. If the bulk population of solute, denoted ρ_2 , is altered by varying H_2 with $H_2 = H_2(S)$, it appears that $\rho_2(0)$ is a very strongly increasing function of ρ_2 . Of course it is not possible to say conclusively whether a phase transition *does* occur from studies of a finite system.

The Monte Carlo simulation of the $10 \times 10 \times 16$ Ising lattice used a Glauber dynamics algorithm. Periodic boundary conditions were applied in x_1, x_2 . The dynamics algorithm for one move was

(i) select a lattice site x at random, which will be in a state $t(x) = 0, 1$ or 2 ,

(ii) Select at random one of the other two states of the site: call this $t'(x)$,

(iii) Change $t(x)$ to $t'(x)$ with probability $[1 + \exp(\beta \Delta E)]^{-1}$ where ΔE is the change in energy of the system when $t(x) \rightarrow t'(x)$.

The lattice contained 1600 sites and the simulation was divided into 'time steps' of 1600 consecutive moves. Most simulation runs were composed of 200 successive time steps though some were 500, 2000 or 10 000. Measurements reported are of averages of the system taken at the end of each time step. In all the simulations reported, $E_{22} = \frac{1}{2}E_{11}$ and $H_1 = 0$. The other energies were parametrised by

$$E_{22}(S) = \alpha E_{11} \quad E_{12} = E_{12}(S) = \gamma E_{11}. \quad (4)$$

The choice of $E_1 = 0$ means that the lattice was always almost filled with solvent with a very low concentration of solute and vacancies in the bulk of the lattice. In table 1 we list the values of ρ_B and $\rho_B(0)$ measured in simulations at the given values of E_{11}, α and γ . For all the results in table 1, $H_2 = 0$.

In figure 1 we plot smooth curves through the data points of $\rho_2(0)$ as a function of α for the cases $E_{11} = 0.9, \gamma = 0.333, H_2 = 0$ and $E_{11} = 0.9, \gamma = 0.444, H_2 = 0$. Notice that

Table 1. Results of simulations for $H_2 = 0$.

E_{11}	γ	α	$\rho_2(0)$	ρ_2	α	$\rho_2(0)$	ρ_2	α	$\rho_2(0)$	ρ_2	
0.555	0	1.08	0.186	0.063	1.26	0.281	0.059	1.43	0.400	0.060	
		1.62	0.792	0.060	1.80	0.910	0.064	1.98	0.943	0.064	
0.6	0	*	1.17	0.145	0.043	1.33	0.247	0.042	1.5	0.660	0.042
			1.67	0.889	0.042	1.83	0.947	0.041			
	0.167		1.17	0.272	0.077	1.33	0.402	0.077	1.5	0.701	0.076
			1.67	0.874	0.078	1.83	0.935	0.078	2.0	0.964	0.078
	0.333		1.17	0.386	0.134	1.33	0.576	0.133	1.5	0.703	0.131
			1.67	0.850	0.129	1.83	0.923	0.135			
0.675	0.148	*	1.04	0.145	0.045	1.18	0.191	0.046	1.33	0.409	0.047
			1.48	0.856	0.047	1.63	0.927	0.043	1.78	0.959	0.045
	0.296		1.04	0.246	0.079	1.19	0.298	0.083	1.33	0.493	0.082
			1.48	0.786	0.080	1.63	0.903	0.081			
0.75	0.267	*	1.07	0.152	0.050	1.2	0.226	0.050	1.33	0.555	0.049
			1.47	0.859	0.049	1.6	0.932	0.049			
	0.4		1.07	0.278	0.089	1.2	0.382	0.091	1.33	0.627	0.091
			1.47	0.832	0.091	1.6	0.900	0.091			
0.9	0.333	*	1.11	0.128	0.033	1.22	0.140	0.034	1.33	0.484	0.035
			1.44	0.908	0.035	1.55	0.953	0.035			
	0.444		1.11	0.277	0.059	1.22	0.416	0.064	1.33	0.751	0.060
			1.44	0.888	0.062	1.55	0.946	0.062			
1.2	0.333	*	1.17	0.061	0.011	1.25	0.190	0.009	1.33	0.320	0.010
			1.42	0.979	0.010	1.50	0.965	0.009			
	0.5		1.08	0.171	0.033	1.17	0.217	0.036	1.25	0.530	0.035
			1.33	0.788	0.034	1.42	0.960	0.032			

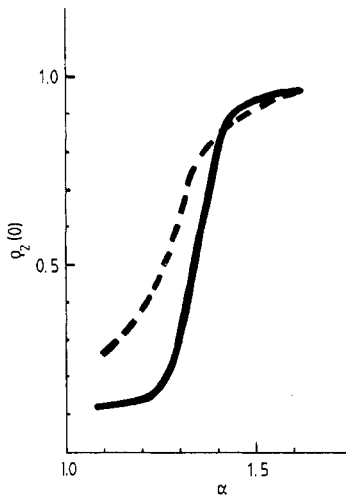


Figure 1. Graphs of $\rho_2(0)$ against α for $E_{11} = 0.9$, $H_2 = 0$: —, $\gamma = 0.333$; ---, $\gamma = 0.444$.

for the case $\gamma = 0.333$, $\rho_2(0)$ varies very sharply with α at $\alpha \approx 1.3$ while when γ increases to 0.444 this variation is much less sharp. This sharp variation indicates highly cooperative behaviour as α varies at small γ while as γ increases the evidence of cooperativity decreases.

It is tempting to identify the behaviour of $\rho_2(0)$ as α varies for $\gamma = 0.333$ as evidence of a surface phase transition. Entries in table 1 marked with an asterisk indicate that the maximum slope in curve of the $\rho_2(0)$ against α was greater than that found at $E_{11} = 0.9$, $\gamma = 0.444$ and $H_2 = 0$.

An important question is the reliability of the measurements made in the simulations, that is, how well does the finite lattice mimic an infinite system and how well has the simulation averaged over the phase space available to the system. It is difficult to judge these matters when there are no exact results available for the model as is the case here.

On the point of system size, we refer to some recent simulations of surface phenomena in a two-dimensional system for which exact results were available (Abraham 1980, Abraham and Smith 1981). These, a 65×65 (4225 sites) system, gave excellent agreement with known exact results. The lattice used here was of the same order of magnitude (38%) as the two-dimensional one considered.

On the other point we note the following.

(i) 10 000 time step runs for a few points gave values of $\rho_2(0)$ not distinguishable on figure 1 from the curves given by more than one thickness of the lines drawn on the graphs.

(ii) The average density of solute in the layer $x_3 = i$, $\rho_2(i)$ varied by less than 10% over the layers $x_3 = 4 - 13$.

(iii) The average density of species 1 in the layer $x_3 = i$, $\rho_1(i)$ was remarkably insensitive to i (variation of less than 1% over $x_3 = 4 - 13$).

(iv) The simulations were done by starting at the highest (or lowest) value of α reported and decreasing (increasing) α , starting a run at a given α from the last configuration of the run at the previous value of α . For $E_{11} = 0.6$, $\gamma = 0$ and $\gamma = 0.333$ and $H_2 = 0$, the data represent two sets of runs, one with increasing α followed by one with decreasing α . No hysteresis effects were observed (again to the accuracy represented by the thickness of the lines in the graphs of figure 1).

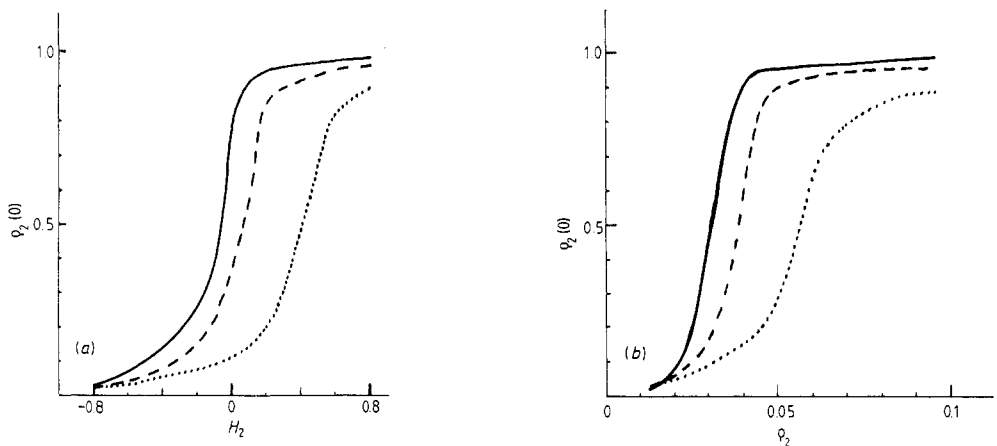


Figure 2. (a) Graph of $\rho_2(0)$ against H_2 for $E_{11} = 0.9$, $\gamma = 0.333$: —, $\alpha = 1.444$; ---, $\alpha = 1.278$; ..., $\alpha = 1.111$. (b) Graph of $\rho_2(0)$ against $\rho_2 E_{11} = 0.9$, $\gamma = 0.333$: —, $\alpha = 1.444$; ---, $\alpha = 1.278$; ..., $\alpha = 1.111$.

We may conclude that the cooperative effects reported here were stable with regard to the number of time steps used and to whether α was increasing or decreasing. The number of time steps used (generally 200) thus seems large enough to give reliable results for this system while remaining small enough for the simulations reported to have been possible.

We now turn to the role of H_2 which controls the bulk solute density ρ_2 . In figure 2(a) we plot $\rho_2(0)$ as a function of H_2 for $E_{11} = 0.9$, $\gamma = 0.33$ and $\alpha = 1.444$, 1.278 and 1.111 and in figure 2(b) we plot $\rho_2(0)$ as a function of ρ_2 for these values of E_{11} , γ and σ . For $\alpha = 1.444$ and 1.278, the system displays highly cooperative effects while cooperativity appears to have decreased considerably for $\alpha = 1.111$. Note also that for $\alpha = 1.111$, the value of H_2 required to increase $\rho_2(0)$ to 0.7 is about 0.5 (cf 0 or 0.1 for $\alpha = 1.444$ or 1.278).

References

- Abraham D B 1980 *Phys. Rev. Lett.* **44** 1165
Abraham D B and Smith E R 1981 *J. Phys. A: Math. Gen.* **14** to be published
Binder K and Hohenberg P 1972 *Phys. Rev. B* **6** 3461
—1974 *Phys. Rev. B* **9** 2194
Domb C 1972 *Phase Transitions and Critical Phenomena* vol 3, ed C Domb and M S Green (London: Academic)