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LETTER TO THE EDITOR

Phase transition in a lattice gas with extended hard core

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Abstract. Numerical results have been obtained by several methods for a hard core two-dimensional lattice gas on a plane-square lattice, involving exclusion of first, second and third neighbours. They strongly suggest the existence of a first-order phase transition.

The existence of phase transitions in lattice gases with hard cores has been extensively investigated since the late sixties and recent contributions by Baxter (1980) on the *interactions-round-a-face* model (IRF) have revived interest in the field. While it seems fairly well established that systems with exclusions limited to first-neighbouring sites display a lambda-type transition, the nature of the transitions occurring in models involving a more extended hard core is still unclear and it is the aim of this paper to analyse one particular model of that type.

The molecules are placed on a plane square lattice; the presence of one of them on a particular site forbids the simultaneous occupancy of that same site and of its first, second and third neighbours, by another molecule. This model was studied previously by Bellemans and Nigam (1966, 1967) and by Bellemans and Orban (1966) through various numerical methods, with the conclusion that it presents a rather strong phase change. Subsequently, the *existence* of a transition was rigorously proved by Heilmann and Praestgaard (1974), although its nature remained undefined. We present below some new numerical data which, in our opinion, suggest this transition to be a first-order one.

The matrix method of Kramers and Wannier is a very practical one for studying 'cylindrical' lattices of infinite length and finite circumference of n sites, in an exact way (from the numerical point of view). Due to the particular shape of the core, n has to be here a multiple of 5, in order to allow the system to reach the close-packing configuration at infinite pressure. The cases $n = 5$, 10 and $n = 15$ were respectively considered by Bellemans and Nigam (1966) and Bellemans and Orban (1966). We have now extended the computations to the case $n = 20$. Note that the dimension of the matrices involved is, in principle, equal to the total number of configurations allowed on a double ring of sites; however, the largest eigenvalue (which is the only relevant one) may be obtained from a reduced matrix, the dimension of which is equal to the total number of classes of equivalent configurations (under rotation and inversion). From the data listed in table 1, it is quite clear that the case $n = 25$ is presently out of reach.

Figure 1 shows the pressure p plotted against the density ρ, for $n = 5$, 10, 15 and 20, while figure 2(a) shows $kT\ \partial\rho/\partial\mu$ (i.e. essentially the compressibility) against the

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Table 1. Number of configurations and of symmetry classes for single and double rings of n sites.

n	Single ring Configurations	Single ring Classes	Double ring Configurations	Double ring Classes
5	6	2	21	4
10	46	6	441	34
15	309	19	9 327	353
20	2090	75	196 333	5140

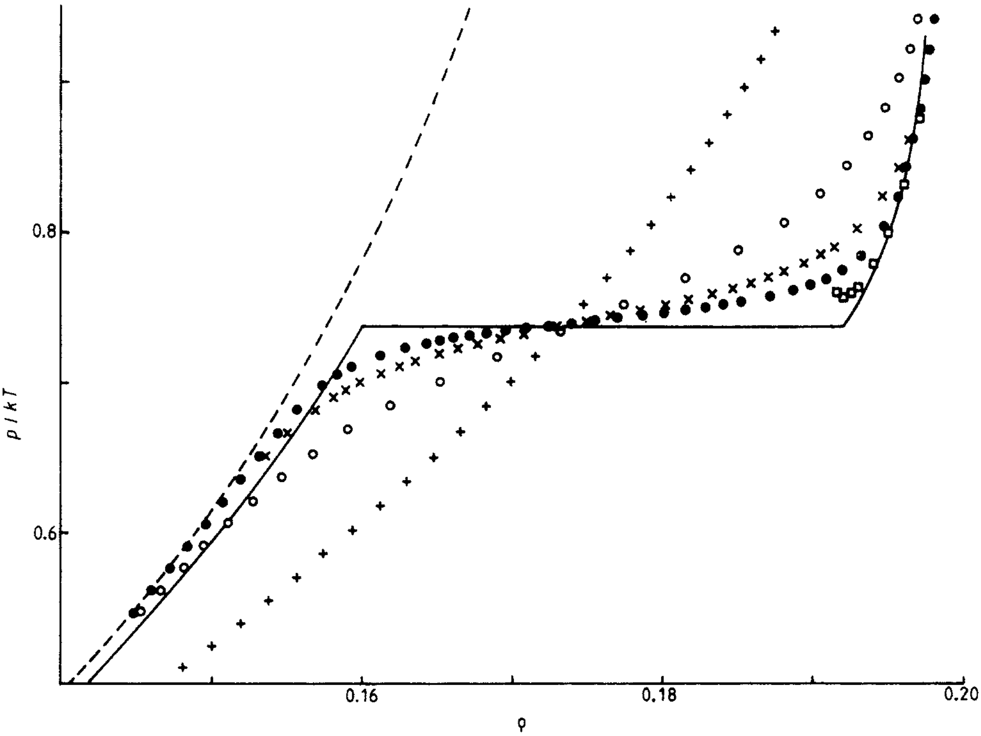

Figure 1. Plot of p/kT against ρ. Matrix method: ●, $n=20$; ×, $n=15$; ○, $n=10$; +, $n=5$. □, High density [1/1] Padé approximant; – – –, low density [5/5] Padé approximant; ——, Rushbrooke–Scoins method.

chemical potential μ. As n increases, there is a substantial flattening of that part of the pressure curve extending between $\rho \simeq 0.16$ and 0.19 (close packing density: $\rho_{\max} = \frac{1}{5}$); this corresponds in turn to a peak in $kT\,\partial\rho/\partial\mu$ which sharpens extremely rapidly with n. Table 2 summarises some characteristic data of that peak for $n=10$, 15 and 20 (the case $n=5$ shows no peak and is therefore omitted). The first three entries specify its location (μ, p, ρ) which seems to vary little with n. The fourth entry gives the height of the peaks shown in figure 2(a): it increases dramatically with n, almost like n^2. At the same time, the width of the peaks, estimated by means of the difference between the chemical potentials μ_{left}, μ_{right}, corresponding to their left and right inflexion points (fifth and sixth entries of table 2), shrinks almost like n^{-2}. It

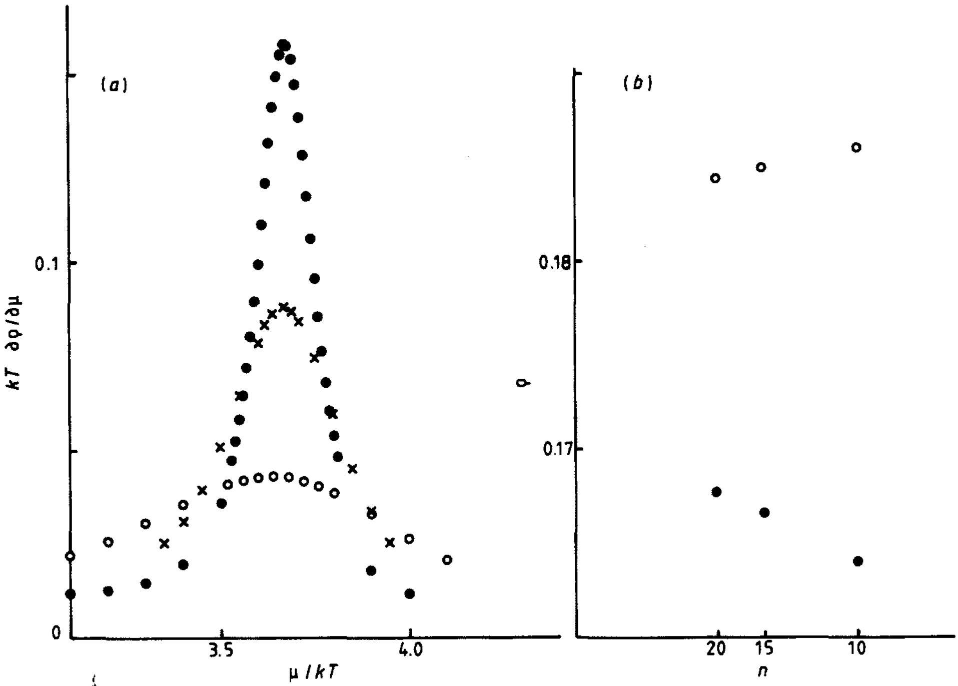

Figure 2. (a) Plot of $kT\ \partial\rho/\partial\mu$ against μ/kT (matrix method; ●, $n=20$, ×, $n=15$, ○, $n=10$). (b) Plot of ρ_{left} and ρ_{right} against $1/n$ (● left, ○ right).

Table 2. Thermodynamic properties associated with the compressibility peak.

n	μ/kT	p/kT	ρ	$kT\ \partial\rho/\partial\mu$	$(\mu/kT)_{\text{left}}$	$(\mu/kT)_{\text{right}}$	ρ_{left}	ρ_{right}
5	—	—	—	—	—	—	—	—
10	3.635	0.7405	0.1746	0.0430	3.366	3.931	0.1640	0.1860
15	3.668	0.7426	0.1757	0.0879	3.554	3.786	0.1666	0.1850
20	3.674	0.7424	0.1761	0.1580	3.615	3.733	0.1677	0.1844
RS method	3.640	0.738	density gap for $0.160<\rho<0.192$ (Bellemans and Nigam 1967)					

seems therefore that these peaks, keeping their surface approximately constant, might rapidly evolve towards a delta function as $n\to\infty$, which would implicate a first-order phase transition. At any rate, the dependence in n observed here disagrees completely with what is known for two-dimensional lattice models exhibiting a lambda transition: in such cases, the maximum height of $kT\ \partial\rho/\partial\mu$ grows like $\ln n$, i.e. much more slowly (Runnels 1965). Furthermore, the densities ρ_{left}, ρ_{right} (last two entries of table 2), corresponding respectively to μ_{left}, μ_{right}, should extrapolate to the same value for $n\to\infty$, if the transition was of the lambda type. This is very unlikely as shown in figure 2(b), where these quantities are plotted against n^{-1}. (On the other hand, μ_{left} and μ_{right} should converge to the same value as $n\to\infty$, whatever the nature of the transition, and indeed, by plotting them against n^{-2}, they both appear to tend to 3.67–3.70.)

Another clue for discriminating between first-order and lambda transitions is the following: the points of maximum curvature, B_1, B_2 of the ρ against μ curve (in reduced units ρ/ρ_{max}, μ/kT) behave very differently as n becomes infinite, as shown in figure 3: (i) for a first-order transition, their abscissae (chemical potentials) become identical and the curvatures infinite, (ii) for a lambda transition, their abscissae remain distinct and the curvature finite. Table 3 gives the chemical potentials, densities and curvatures of B_1, B_2 for $n = 10$, 15 and 20. On the one hand, μ_1 and μ_2 values, when plotted against n^{-2}, extrapolate quite nicely towards 3.68_2 and 3.69_0 respectively; on the other hand, the curvatures grow extremely rapidly with n, almost like n^4. This provides reasonable evidence, in our opinion, for a first-order transition.

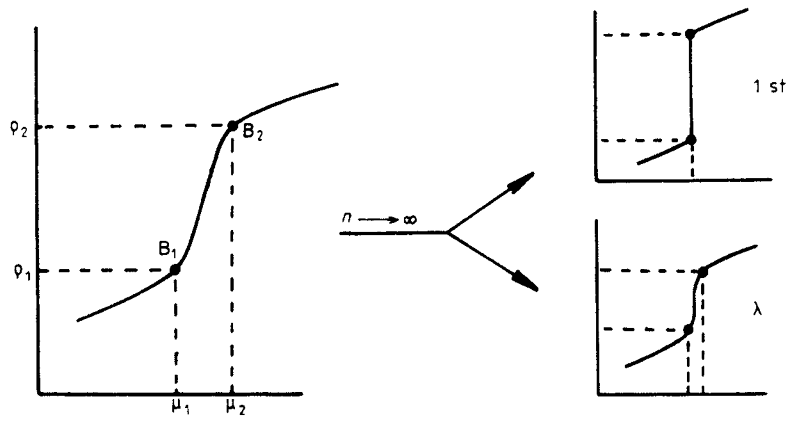

Figure 3. Schematic plot of the evolution of the ρ against μ curve as n goes to infinity, for first-order and lambda transitions respectively (B_1, B_2 are points of maximum curvature).

Table 3. Points of maximum curvature along the ρ/ρ_{max} against μ/kT curve (points B_1, B_2 of figure 3).

n	μ_1/kT	ρ_1	Curvature	μ_2/kT	ρ_2	Curvature
10	3.3600	0.1638	0.2475	3.9282	0.1862	0.3053
15	3.5428	0.1659	1.262	3.7975	0.1857	1.353
20	3.5992	0.1660	3.717	3.7492	0.1861	3.850

A different approach to the problem of hard core lattice gases, originated by Gaunt and Fisher (1965), makes use of low and high activity or density series. The usual cluster sums b_l and β_k, involved respectively in low activity and density expansions, were previously derived up to $l = 5$ and $k = 4$ by Bellemans and Nigam (1967); we have extended them up to $l = 11$ and $k = 10$; see table 4. Similarly the coefficients a_l and α_k involved in the high activity and density expansions, i.e.

$$p/kT = \tfrac{1}{5}(\ln z + \textstyle\sum a_l z^{-l}), \qquad z = \exp(\mu/kT),$$

$$p/kT = \tfrac{1}{5}(-\ln x + \textstyle\sum \alpha_k x^k), \qquad x = 1 - 5\rho,$$

have been evaluated up to $l = 4$ and $k = 3$. The [5/5] and [1/1] Padé approximants,

Table 4. Coefficients of the high and low density expansions (α_k and β_k) and of the high and low activity expansions (a_l and b_l) of the pressure.

k or l	$5\,\alpha_k$	$5la_l$	$k\beta_k$	lb_l
1	12	1	−13	1
2	12	11	−97	−13
3	236	199	−553	205
4		4567	−2 781	−3 521
5			−13 873	63 466
6			−74 341	−1 180 075
7			−427 321	22 423 304
8			−2 491 549	−432 957 233
9			−14 068 453	8 463 267 016
10			−75 888 787	−167 059 758 328
11				3 323 928 207 970

in ρ and x respectively, are shown in figure 1; their behaviour again suggests the equation of state to consist of two different branches separated by a density gap, between $\rho \simeq 0.16$ and 0.19.

To be complete, figure 1 includes the p against ρ curve obtained by Bellemans and Nigam (1967) by means of the Rushbrooke–Scoins method (see also last line of table 2).

Several observations have been made above, all of them pointing towards the existence of a density gap in the equation of state of the model. Although none of them may be considered as a *proof*, we nevertheless shall conclude, to a high degree of confidence, that this model exhibits a first-order transition, which recalls the one occurring for hard spheres.

Similar investigations are under way for other lattice models of the same kind.

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