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1982 J. Phys. A: Math. Gen. 15 1327

(http://iopscience.iop.org/0305-4470/15/4/032)

J. Phys. A: Math. Gen. **15** (1982) 1327–1338. Printed in Great Britain

Phase transitions in the square well and hard ramrod lattice gases

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Received 21 September 1981

Abstract. A numerical investigation of the two-dimensional square well lattice gas and a gas of hard ramrods has been carried out using the scaling transformation. Both models appear to exhibit a single Ising-model-like second-order phase transition over the whole temperature range.

1. Introduction

In a previous publication on vertex model representations of lattice gas models (Wood and Goldfinch 1980) the authors have shown that the scaling transformation (Nightingale 1976) can be a very powerful numerical method for obtaining all of the critical parameters associated with the phase transitions of lattice gas models. When this method was applied to the two-dimensional hard square lattice gas it gave extremely sharp evidence that this model has a single fluid–solid-like second-order phase transition, which is of the same class as the two-dimensional Ising model. A strong feature of the method is the relative ease with which the interaction details of such model Hamiltonians can be altered, and the automatic transfer between successive levels of approximation.

In the present paper we have applied the scaling transformation to a pair of two-dimensional lattice gas models, both of which contain a symmetric hard core extending over a nearest-neighbour distance. For comparison we have duplicated all of our results for the Ising model lattice gas of Yang and Lee (1952) with purely repulsive forces. The latter model is of course the Ising model of an antiferromagnet in a field, and the results given here can be mapped onto the corresponding transition line (H_c, T_c); recently an estimate of this line has been obtained by Sneddon (1979) also using a scaling transformation†. The two models are Fisher's super-exchange lattice gas (Fisher 1963), which can also be viewed as a gas of hard ramrods of arbitrary length (see Wood and Goldfinch 1980 and below), and the square well lattice gas (Runnels *et al* 1970). All of the models in this paper have a characteristic and finite interaction potential parameter, and we shall use the same symbol φ to denote this parameter in each model; $\varphi > 0$ and $\varphi < 0$ correspond to repulsive and attractive forces, respectively, throughout.

† We believe that the precision of the present calculations shows there to be substantial deviations from the conjectured exact form of the transition line (H_c, T_c) put forward by Muller-Hartmann and Zittartz (1977). These deviations increase as one moves away from the Ising model critical point $(0, T_c)$. This has also been noted by Baxter *et al* (1980).

0305-4470/82/041327+12$02.00

Several authors have studied lattice gas models for which in addition to a symmetric hard core there exists an attractive range beyond the core (Orban and Bellemans 1968, Orban *et al* 1968, Runnels *et al* 1970, for a review see Runnels 1972). In both approximate and exact work (Gaunt and Fisher 1965, Gaunt 1967, Baxter *et al* 1980, Baxter 1980, Wood and Goldfinch 1980) it is clear that a symmetric hard core will promote a single second-order phase transition, which is really of a gas–solid type. Previous authors have speculated that a third liquid-like phase could be obtained from a Hamiltonian which contained a range of attraction beyond the hard core. Thus Fisher's super-exchange gas on the square net lattice has a nearest-neighbour (NN) hard core with an interaction potential φ across next-nearest-neighbour (NNN) distances but only within alternate squares of the lattice (the white squares on a chess board say). This contrived model is of interest because it can be solved exactly at one and only one value of the temperature given by $\exp(-\beta\varphi) = 2$, at which point the model has one Ising-like second-order transition. Fisher speculated that in the attractive domain $\varphi < 0$ ($\varphi = 0$ is the case which is equivalent to the hard square gas) the transition would remain of the Ising model type throughout the whole temperature domain.

Runnels *et al* (1970) using the so-called exact finite method completed Fisher's model by including the potential φ across all of the squares of the net, thus forming the square well lattice gas. These authors in a qualitative interpretation of their isothermals obtained on finite systems concluded that in the attractive domain $\varphi < 0$ there was a single transition which at low temperatures was first order, possibly turning to second order at higher temperatures.

In our study of these models we find that Fisher's speculation is verified at all temperatures but that Runnels *et al* appear to have been misled by their data; the square well gas seems to have one second-order transition at all temperatures, which like the super-exchange gas remains Ising-model-like everywhere.

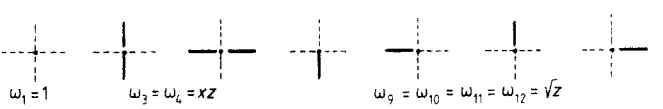
2. Models and representations

Consider the square net lattice sites labelled $i = 1, 2, \ldots, N$ to have site variables $t_i = 1$ (0) if an atom is present (or absent) at the site; then the two hard core lattice gas models in this work have a grand partition function Ξ given by

$$\Xi = \sum_{\{t\}} \prod_{(ab)} (1 - t_a t_b) \prod_{(aa')} x^{t_a t_{a'}} \prod_{(bb')} x^{t_b t_{b'}} \prod_{(a)} z^{t_a} \prod_{(b)} z^{t_b} \tag{1}$$

where z is the activity and $x = \exp(-\beta\varphi)$. The lattice has been divided into its two sublattices denoted here by a sites and b sites (each a site is surrounded by four b sites), thus in (1) (ab) runs over all NN pairs of sites and (aa') and (bb') run all over NNN pairs of sites for the square well gas, *but* over all such pairs in 'white' squares only for the super-exchange gas.

Following Wood and Goldfinch (1980) the super-exchange gas can be made equivalent to a special case of the sixteen-vertex model on the square net lattice in which the non-zero vertex weights are



(2)

A typical configuration of such a vertex model is shown in figure 1, hence the name

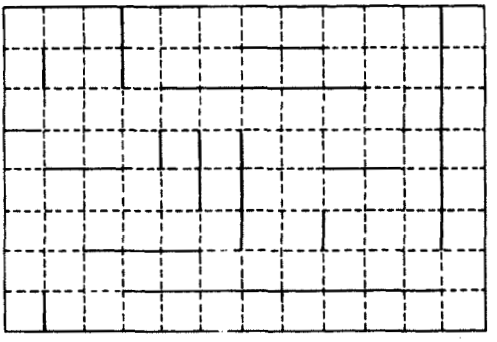


Figure 1. A configuration of the lattice ramrod model.

ramrod model (first given by Nagle 1968); clearly the model is equivalent to a mixture of hard rods of arbitrary length which can assume horizontal or vertical positions. Alternatively it is a gas of dimers with 'sticky' ends, which can join end on through the potential φ.

There seems to be no simple vertex model form for the square well gas, which is probably best viewed as a gas on square molecules with sticky sides as illustrated in figure 2. The scaling transformation identifies a second-order phase transition through the solutions of the equation

$$n\xi_{m,\infty}(z, x) = m\xi_{n,\infty}(z, x) \tag{3}$$

at critical points $z_c(n, m)$, $x_c(n, m)$. Here $\xi_{k,\infty}$ is the correlation length obtained from a toroidal $k \times \infty$ square net, and $z_c(n, m)$ is an approximant to the true critical activity $z_c(\infty, \infty)$ where $\xi_{\infty,\infty}$ diverges. The correlation lengths are obtained in the usual way via the relation

$$\xi_{m,\infty} = 1/\ln(\lambda_1(m)/|\lambda_2(m)|) \tag{4}$$

where $\lambda_1(m)$ and $\lambda_2(m)$ are the largest and next largest (in modulus) eigenvalues of a transfer matrix established between adjacent columns of m sites in the $m \times \infty$ toroidal lattice. The correlation length critical exponent ν is obtained as a sequence of approximants $y(n, m)$ $(y = 1/\nu)$ given by

$$(m/n)^{y(n,m)} = (n/m)\xi_z(m, \infty)/\xi_z(n, \infty) \qquad z = z_c(n, m) \tag{5}$$

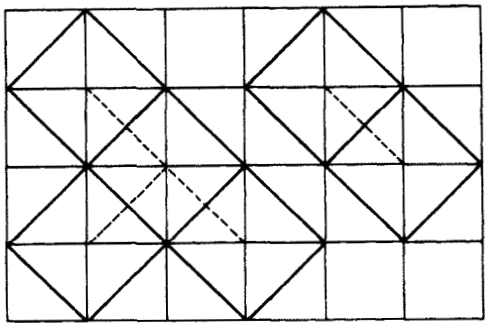


Figure 2. A configuration in the square well gas; interactions act along the broken lines.

where the z subscript signifies the partial derivative (see Wood and Goldfinch (1980) for further details).

The transfer matrix for the square well gas was established directly in terms of the site variables, thus if $\boldsymbol{t}$ and $\boldsymbol{\tau}$ represent the m site variables on neighbouring columns of the $m \times \infty$ system, then a $2^m \times 2^m$ transfer matrix is given by

$$T(\boldsymbol{t}:\boldsymbol{\tau}) = \prod_{i=1}^{m} (1-t_i t_{i+1})(1-\tau_i \tau_{i+1})(1-t_i \tau_i) \prod_{i=1}^{m} x^{(t_i \tau_{i-1} + \tau_i t_{i-1})} z^{\frac{1}{2}\sum(t_i+\tau_i)}. \tag{6}$$

In the computational scheme for the super-exchange gas we have followed the vertex model form in (2) which has a transfer matrix in the form

$$T(\sigma:\sigma') = \sum_{C_v} P(C_v) \tag{7}$$

where σ and σ' represent the states of the neighbouring horizontal bonds and C_v is a configuration of the intervening vertical bonds (again a $2^m \times 2^m$ matrix), thus σ, σ' and C_v define a complete column of vertices, and $P(C_v)$ is the product of the vertex weights in (2) down this column.

Using the transfer matrices in (6) and (7) numerical solutions to (3) have been obtained to yield approximant sequences $z_c(m, n)$, and $\nu(m, n)$ over a range of values of the reduced temperature $kT/|\varphi|$. Thermodynamic properties at critical points can easily be found by numerically forming the appropriate thermodynamic relation using the maximum eigenvalue for the largest strip and using the 'best' values for the critical point z_c. The critical pressure and density curves shown below have been obtained in this way, and here of course the method makes contact with the earlier work using the exact finite method (Runnels 1972).

3. Critical thermodynamic properties

The full scale of our calculations is illustrated here for the ramrod gas; the numerical results for this model are given in tables 1–4 and include both attractive and repulsive forces ($\varphi < 0$, and $\varphi > 0$ respectively). The critical density and pressure values which are given in tables 3 and 4 are adapted to fit the ramrod model, which clearly has a maximum packing density of 1; the critical densities and pressures for the corresponding super-exchange gas are half of the quoted values. The ramrod model is useful to us here in that it provides a good check on the numerical accuracy of the results at two points; $x = 1$ is the hard square gas, and $x = 2$ is Fisher's exactly solvable point in the super-exchange gas. These points are marked in the tables and the accuracy of the scaling calculations in each case is excellent. In the range $1 < x < 2$ we clearly expect that this level of accuracy will be maintained. The bottom row in tables 1 and 2 corresponds to applying a simple optimal extrapolation fit (similar to Nightingale (1976)) to some of the sequences (n, m) and we expect that these figures will be within one per cent of the exact results over most of the tables.

Fisher's conjecture that his model would exhibit a single Ising-model-like phase transition at all temperatures is quite clearly correct, and indeed appears to extend into the repulsive domain. The corresponding numerical results which we have obtained for the square well lattice gas and the repulsive force Ising model lattice gas of Yang and Lee (1952) are listed in tables 5 and 6, but here we list only the best estimates corresponding to the bottom rows in the earlier tables for the ramrod model. In their

Table 1. Values of z_c obtained from the approximants $z_c(n, m)$ in solutions to (3) at various values of the reduced temperature in terms of $x = \exp(-\beta\varphi)$.

x	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.5	2.0	2.5	3.0	3.5
n, m	Repulsive forces $\varphi > 0$							$\varphi = 0$	Attractive forces $\varphi < 0$				
3, 2	35.06	19.81	12.77	8.960	6.669	5.187	4.173	3.449	1.729	1.104	0.7956	0.6146	0.4966
4, 2	34.36	19.64	12.79	9.053	6.785	5.306	4.285	3.551	1.780	1.127	0.8057	0.6185	0.4975
4, 3	33.55	19.45	12.82	9.154	6.910	5.431	4.403	3.657	1.832	1.151	0.8160	0.6240	0.4983
5, 2	34.24	19.66	12.86	9.128	6.861	5.377	4.351	3.611	1.812	1.144	0.8150	0.6237	0.5005
5, 3	33.75	19.57	12.90	9.219	6.965	5.480	4.446	3.696	1.855	1.165	0.8250	0.6284	0.5024
5, 4	33.96	19.69	12.99	9.287	7.022	5.529	4.490	3.735	1.869	1.174	0.8311	0.6327	0.5056
6, 2	34.18	19.68	12.90	9.178	6.910	5.423	4.393	3.648	1.833	1.156	0.8220	0.6281	0.5033
6, 3	33.84	19.63	12.95	9.258	6.998	5.508	4.471	3.718	1.869	1.174	0.8311	0.6327	0.5056
6, 4	33.99	19.73	13.02	9.313	7.044	5.548	4.506	3.750	1.888	1.186	0.8389	0.6379	0.5093
6, 5	34.02	19.76	13.05	9.338	7.066	5.567	4.524	3.765	1.897	1.193	0.8437	0.6415	0.5120
7, 2	34.16	19.70	12.93	9.313	6.944	5.454	4.421	3.673	1.184	1.165	0.8272	0.6314	0.5056
7, 3	33.90	19.67	12.98	9.284	7.019	5.527	4.488	3.733	1.878	1.180	0.8353	0.6357	0.5079
7, 4	34.02	19.75	13.03	9.329	7.058	5.560	4.517	3.759	1.894	1.191	0.8420	0.6403	0.5112
7, 5	34.05	19.77	13.06	9.350	7.076	5.576	4.531	3.772	1.902	1.196	0.8460	0.6433	0.5134
7, 6	34.07	19.79	13.07	9.362	7.086	5.585	4.539	3.778	1.906	1.199	0.8483	0.6451	0.5149
Extrapolation	34.04	19.80	13.10	9.372	7.118	5.613	4.564	3.801	1.923	1.215	0.8655	0.6650	0.5403
Exact								3.796[a]		1.207[b]			

[a] Baxter *et al* (1980)
[b] Fisher (1963).

Table 2. Values of the correlation length exponent $y(n, m)$ $(=1/\nu(n, m))$ obtained from (5) for the ramrod model.

x	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.5	2.0	2.5	3.0	3.5
n, m	Repulsive forces $\varphi > 0$							$\varphi = 0$		Attractive forces $\varphi < 0$			
3, 2	1.353	1.289	1.234	1.189	1.153	1.124	1.102	1.087	1.064	1.079	1.102	1.122	1.140
4, 2	1.239	1.198	1.163	1.135	1.115	1.095	1.082	1.072	1.058	1.070	1.089	1.107	1.124
4, 3	1.069	1.067	1.064	1.062	1.060	1.056	1.054	1.053	1.051	1.059	1.072	1.086	1.101
5, 2	1.190	1.157	1.130	1.108	1.091	1.078	1.068	1.061	1.051	1.062	1.078	1.095	1.110
5, 3	1.055	1.052	1.049	1.047	1.045	1.043	1.042	1.041	1.042	1.049	1.061	1.073	1.086
5, 4	1.036	1.032	1.029	1.028	1.027	1.026	1.026	1.027	1.030	1.037	1.046	1.056	1.067
6, 2	1.161	1.134	1.111	1.093	1.078	1.067	1.059	1.053	1.046	1.056	1.070	1.085	1.100
6, 3	1.044	1.042	1.040	1.038	1.037	1.036	1.035	1.034	1.036	1.043	1.052	1.064	1.075
6, 4	1.027	1.024	1.022	1.021	1.021	1.021	1.021	1.021	1.025	1.031	1.037	1.047	1.057
6, 5	1.016	1.015	1.014	1.014	1.014	1.014	1.014	1.014	1.018	1.023	1.030	1.037	1.045
7, 6	1.009	1.008	1.008	1.008	1.008	1.008	1.008	1.009	1.012	1.016	1.020	1.026	1.032
Extrapolation	1.003	1.002	1.001	1.001	1.001	1.000	1.000	1.000	0.999	0.998	0.996	0.994	0.991
Exact										1.000[a]			

[a] Fisher (1963).

Table 3. Critical densities $\rho_c(n)$ of the ramrod model at temperatures corresponding to table 1, evaluated using $z_c(7, 6)$ at various strip widths n.

x	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.5	2.0	2.5	3.0	3.5
n				Repulsive forces $\varphi > 0$				$\varphi = 0$			Attractive forces $\varphi < 0$		
2	0.7615	0.7588	0.7558	0.7526	0.7493	0.7459	0.7424	0.7389	0.7247	0.7055	0.6906	0.6771	0.6649
3	0.7607	0.7569	0.7532	0.7495	0.7460	0.7424	0.7390	0.7357	0.7198	0.7052	0.6919	0.6796	0.6682
4	0.7601	0.7562	0.7524	0.7487	0.7451	0.7416	0.7381	0.7348	0.7191	0.7050	0.6922	0.6805	0.6697
5	0.7599	0.7560	0.7522	0.7484	0.7448	0.7413	0.7378	0.7345	0.7188	0.7049	0.6922	0.6807	0.6701
6	0.7599	0.7559	0.7521	0.7483	0.7447	0.7411	0.7377	0.7343	0.7186	0.7047	0.6921	0.6807	0.6702
7	0.7598	0.7559	0.7520	0.7483	0.7446	0.7411	0.7376	0.7342	0.7186	0.7046	0.6920	0.6806	0.6701
Exact								0.736 ± 0.002[a]		0.7071[b]			

[a] Baxter *et al* (1980).
[b] Fisher (1963).

Table 4. Critical pressure $\beta P_c(n)$ of the ramrod model at temperatures corresponding to table 1 evaluated using $z_c(7, 6)$ at various strip widths n.

x	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.5	2.0	2.5	3.0	3.5
n				Repulsive forces $\varphi > 0$				$\varphi = 0$			Attractive forces $\varphi < 0$		
2	2.655	2.397	2.203	2.050	1.924	1.818	1.727	1.648	1.366	1.189	1.065	0.9732	0.9022
3	2.614	2.357	2.164	2.011	1.886	1.780	1.689	1.609	1.325	1.145	1.018	0.9230	0.8490
4	2.601	2.344	2.151	1.998	1.873	1.767	1.676	1.596	1.311	1.130	1.003	0.9069	0.8320
5	2.595	2.338	2.145	1.992	1.866	1.761	1.670	1.590	1.365	1.124	0.9961	0.9001	0.8248
6	2.592	2.335	2.142	1.989	1.863	1.757	1.666	1.587	1.302	1.121	0.9927	0.8966	0.8212
7	2.590	2.333	2.140	1.987	1.861	1.755	1.664	1.585	1.300	1.119	0.9907	0.8945	0.8191
Exact								1.590[a]		1.118[b]			

[a] Gaunt and Fisher (1965).
[b] Fisher (1963).

Table 5. Critical parameters corresponding to tables 1–4 for the square well gas.

	Repulsive forces $\varphi > 0$							$\varphi = 0$	Attractive forces $\varphi < 0$				
x	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.5	2.0	2.5	3.0	3.5
z_c	332.4	109.6	46.99	23.78	13.53	8.327	5.481	3.796	0.9917	0.4161	0.2237	0.1393	0.0956
$y = 1/\nu$	1.020	1.012	1.006	1.003	1.002	1.002	1.003	1.002	1.007	0.9990	0.9712	1.082	1.17
ρ_c	0.3898	0.3868	0.3838	0.3806	0.3775	0.3743	0.3712	0.3681	0.3533	0.3404	0.3300	0.3222	0.3165
βP_c	1.822	1.559	1.361	1.203	1.074	0.9665	0.8745	0.7951	0.5211	0.3929	0.2629	0.1962	0.1490

Table 6. Critical parameters for the repulsive force lattice gas Ising model of Yang and Lee (1952). Two phase transitions occur in the domain $x = \exp(-\beta\varphi) < (\sqrt{2}-1)^2$ at the critical activities z_1 and z_2 related by $z_1 z_2 x^4 = 1$.

x	0	0.02	0.04	0.06	0.08	0.10	0.12	0.14	0.16
z_1	3.796	4.164	4.587	5.118	5.807	6.743	8.111	10.37	15.34
$y = 1/\nu$	1.000	0.9790	0.9850	0.9907	0.9977	1.002	1.008	1.014	1.020
ρ_c	0.3681	0.3758	0.3838	0.3925	0.4022	0.4131	0.4258	0.4414	0.4637
βP_c	0.7591	0.8332	0.8735	0.9200	0.9746	1.041	1.124	1.238	1.424

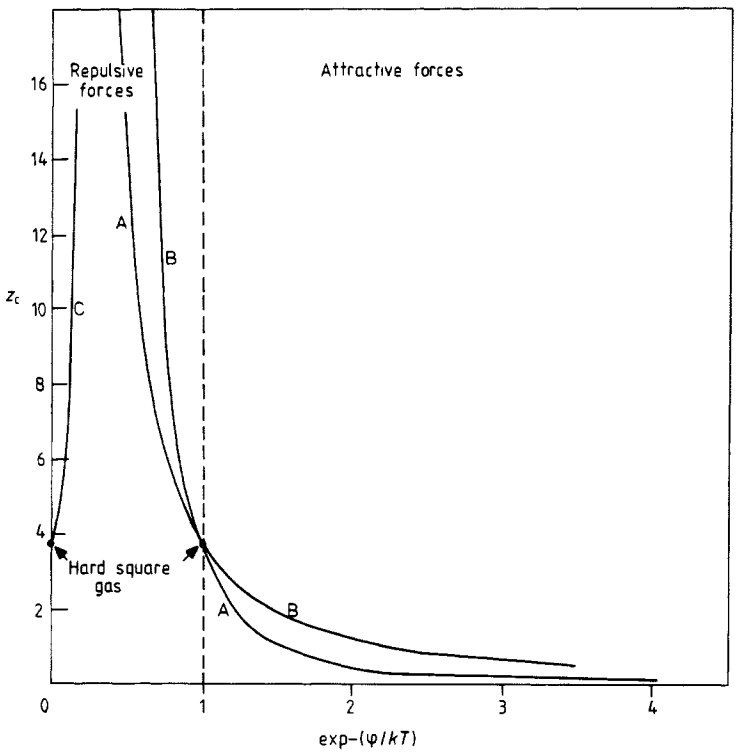


Figure 3. The critical activities of A, the ramrod model; B, the square well gas; C, the repulsive Ising model.

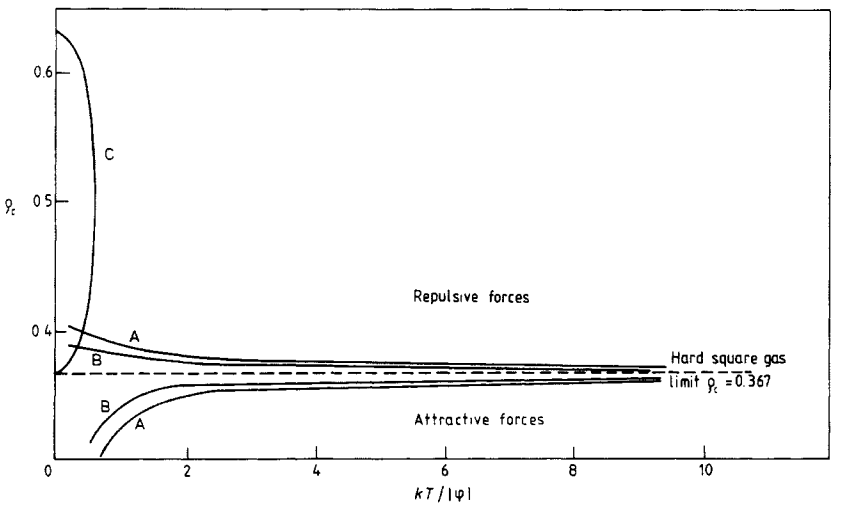


Figure 4. Critical density curves at various values of the reduced temperature for A, the ramrod model; B, the square well gas; C, the repulsive Ising model.

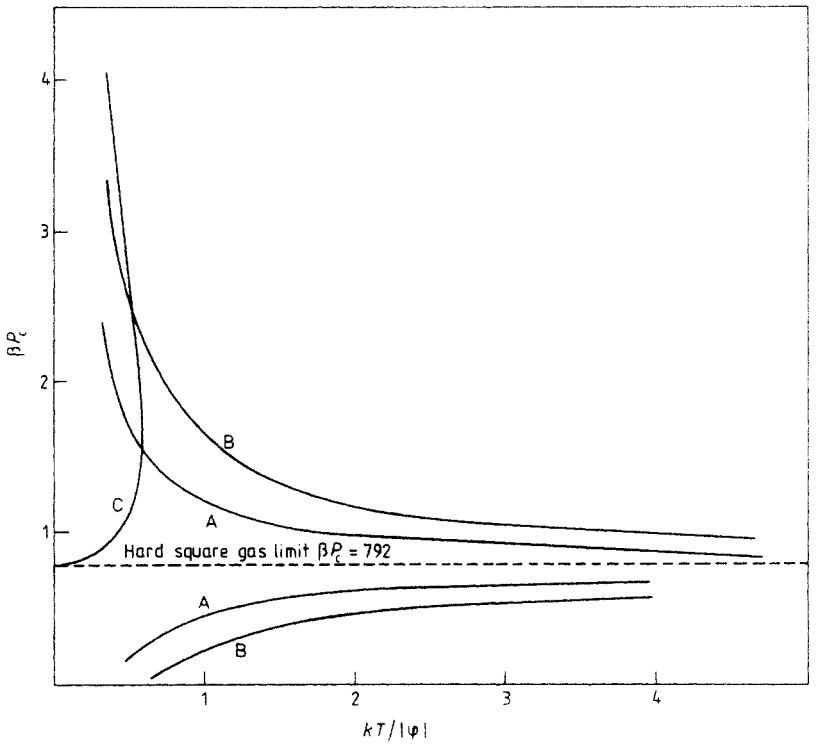


Figure 5. Critical pressure curves for A, the ramrod model; B, the square well gas; C, the repulsive Ising model.

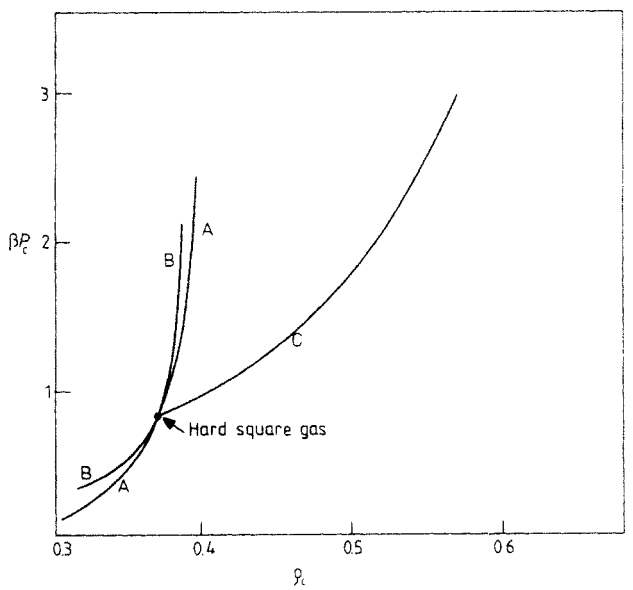


Figure 6. Critical density–pressure curves for A, the ramrod model; B, the square well gas; C, the repulsive Ising model.

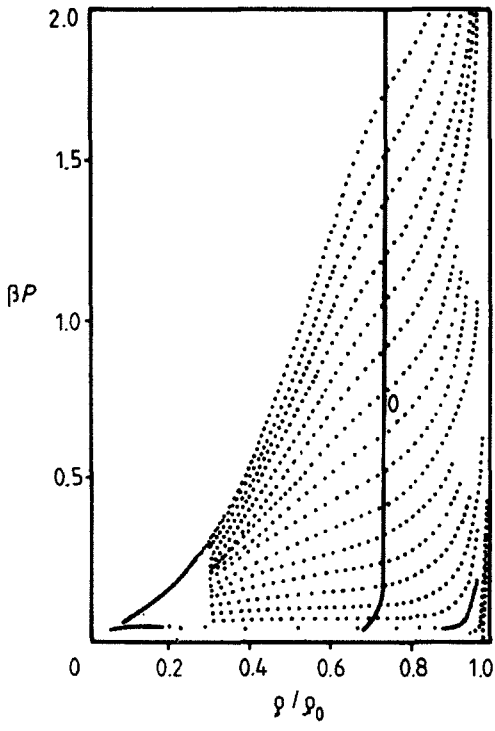


Figure 7. Isothermals for the square well gas, obtained by Runnels *et al* (1970). The isotherm corresponding to the square well gas is marked 0, and the line of second-order transition points found in this work is marked by the full curve.

work on the square well gas Runnels *et al*, using the exact finite method, concluded that the model had one second-order transition at all temperatures in the repulsive domain; this is clearly correct. In the attractive domain the shape of the isothermals led Runnels *et al* to conclude that the system had a first-order transition at low temperatures, and that this might change into a second-order transition at higher temperatures. This conclusion appears to us to be wrong; we think that the scaling calculations here show that the model has just one second-order transition at all temperatures which remains everywhere of the Ising model type. Thus the scaling calculations here show that the super-exchange and square well gases behave in exactly the same way throughout the temperature range both for repulsive and attractive forces.

The results which we have obtained for all three models are compared graphically in figures 3–6, and in figure 7 we have superimposed the critical points ρ_c, P_c onto the original isothermals of Runnels *et al* which they obtained from a toroidal strip with $m = 16$.

Acknowledgments

One of us (MG) would like to thank the SRC for the award of a maintenance grant.

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