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1980 J. Phys. A: Math. Gen. 13 L217

(http://iopscience.iop.org/0305-4470/13/6/011)

J. Phys. A: Math. Gen., 13 (1980) L217–L220. Printed in Great Britain

LETTER TO THE EDITOR

Lattice gas model for liquid–vapour transition: non-singular diameter without particle–hole symmetry

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Received 21 April 1980

Abstract. A lattice gas model for the liquid–vapour transition without particle–hole symmetry and in the Ising universality class is presented. The coexistence curve diameter is an analytic function of temperature. The relation of this model to others which have singular diameters and also to renormalisation group calculations is discussed.

There has been much activity on determining the nature of the singularity in the coexistence curve diameter near the liquid–vapour critical point since the work of Widom and Rowlinson (1970) (WR). The diameter $\rho_D = (\rho_L + \rho_V)/2$ (where ρ_L is the fluid's density in the liquid phase, ρ_V the vapour density) is a measure of the degree of asymmetry in the liquid–vapour transition. Since the usual Ising lattice gas model (Yang and Lee 1952) has a symmetric diameter, $\rho_D \equiv \frac{1}{2}$, one is led to consider models of a more general character which still belong to the Ising universality class (it is generally believed, and confirmed by experiment, that real fluids have Ising exponents (Hayes and Carr 1977, Hocken and Moldover 1976)) and yet produce asymmetry in the diameter. In this Letter we present such a model.

The symmetric diameter of the Ising lattice gas model is a consequence of particle–hole symmetry (Widom and Rowlinson 1970), $n_x \leftrightarrow 1 - n_x$, where $n_x = 0, 1$ is the occupation number of lattice site x. The lack of such a symmetry will have as a consequence a diameter which does not coincide with the critical isochore. It is moreover believed that ρ_D will have a singular temperature dependence: $\rho_D - \rho_c \propto (T_c - T)^{1-\alpha}$ (α is the specific heat exponent). We show on a simple model that this singular dependence is not a necessary consequence of the particle–hole asymmetry.

Our fluid is a lattice analogue of the Widom–Rowlinson model although there is a fundamental difference between them as we shall see later. The atoms are spheres which can occupy sites of a d-dimensional hypercubic lattice. The radius of each sphere is larger than $a/2$, a being the distance between nearest neighbours, but smaller than $a/\sqrt{2}$, so that only spheres which are nearest neighbours can overlap. Each site can accept an arbitrary number of atoms. Let us consider an arbitrary configuration of N spherical atoms and denote by $W(x_1, \ldots x_N)$ the total volume covered by these spheres; $x_1 \ldots x_N$ are the lattice points occupied by the spheres (some x_i's may be the same). Now we define the energy of this configuration as

$$U = \epsilon_0(W(x_1 \ldots x_N) - Nv_0)$$

0305-4470/80/060217+04$01.50

where ϵ_0 is a parameter and v_0 is the volume of the sphere. This expression can be rewritten as

$$U = \epsilon_0\Big(v_0 \sum_x \theta(n_x) - v_1 \sum_{\langle x,x'\rangle} \theta(n_x)\theta(n_{x'}) - v_0 N\Big)$$

where n_x is the number of atoms at the site x, $\theta(n) = 1$ if $n > 0$, $\theta(0) = 0$, v_1 is the overlap volume of two spheres which are nearest neighbours and the symbol $\langle x, x'\rangle$ denotes the bond between two nearest neighbours x and x'. Denoting $\epsilon = \epsilon_0 v_1$, $\mu_0 = \epsilon_0 v_0$, and introducing the chemical potential μ, we get the grand Hamiltonian

$$H = -\epsilon \sum_{\langle x,x'\rangle} \theta(n_x)\theta(n_{x'}) - (\mu + \mu_0)\sum_x n_x + \mu_0 \sum_x \theta(n_x). \tag{1}$$

The grand partition function Z_G is a sum over all configurations $\{n_x\}$ of $\exp(-\mathcal{H})$, where $\mathcal{H}$ is the effective Hamiltonian H/T, with the temperature T measured in energy units. The configuration sum may be rearranged in the following way. There are many microscopic configurations $\{n_x\}$ which correspond to a *fixed* configuration $\{\theta_x\}$. ($\theta_x = 1$ if the site x is occupied by some atoms and $\theta_x = 0$ if the site is empty.) Therefore we first sum over all $\{n_x\}$ for a given $\{\theta_x\}$ and then sum over $\{\theta_x\}$. When the first step is performed, the term $-(\mu + \mu_0)\,\Sigma_x\, n_x$ is replaced by $-\mu_{\text{eff}}(\mu, T)\,\Sigma_x\,\theta_x$ (since $\Sigma_x\,\theta_x$ is the number of occupied sites in the lattice for fixed $\{\theta_x\}$) where

$$\exp(\mu_{\text{eff}}(\mu, T)/T) = (\exp[-(\mu + \epsilon)/T] - 1)^{-1}. \tag{2}$$

Hence the grand partition function is

$$Z_G = \sum_{\{\theta_x\}} \exp(-\bar{\mathcal{H}}) \tag{3}$$

where

$$\bar{\mathcal{H}} = -\frac{\epsilon}{T}\sum_{\langle x,x'\rangle} \theta_x\theta_{x'} - \frac{\bar{\mu}}{T}\sum_x \theta_x \tag{4}$$

and $\bar{\mu}(\mu, T) = \mu_{\text{eff}}(\mu, T) - \mu_0$. We see that $\bar{\mathcal{H}}$ is the Ising lattice gas model in the θ_x variables. For convenience we change to Ising spins $s_x = 2\theta_x - 1$ ($s_x = \pm 1$). Then the thermodynamic potential per site is

$$\omega = -\tfrac{1}{2}(\bar{\mu} + \tfrac{1}{4}z\epsilon) + \omega_{\text{Ising}} \tag{5}$$

where z is the number of nearest neighbours and ω_{Ising} is the thermodynamic potential of the Ising model with 'external field'

$$h = (1/2T)(\bar{\mu} + \tfrac{1}{2}z\epsilon) \tag{6}$$

and coupling constant $K = \epsilon/4T$. The density of particles per site, $\rho = -(\partial\omega/\partial\mu)_T$, as a function of (μ, T) is then

$$\rho(\mu, T) = \tfrac{1}{2}(1 - \exp[(\mu + \mu_0)/T])^{-1}(1 + \langle s_x\rangle_{\text{Ising}}) \tag{7}$$

where $\langle s_x\rangle_{\text{Ising}}$ is the magnetisation per site in an external field.

The coexistence boundaries may now be determined. In the two-phase region, $T < T_c$, the coexistence curve is given by a segment of the line $h = 0 = \bar{\mu} + \frac{1}{2}z\epsilon$. In the (μ, T) plane this is the analytic curve $\mu = -\mu_0 - T\ln(1 + \exp[(z\epsilon - 2\mu_0)/2T])$. Hence on the coexistence curve, the boundaries of the two-phase region in the (ρ, T) plane are

$$\rho_\pm(T) = \tfrac{1}{2}(1 + \exp(-z\epsilon'/2T))(1 \pm m(T)) \tag{8}$$

where $z\epsilon' \equiv z\epsilon - 2\mu_0$ and $m(T)$ is the spontaneous magnetisation of the Ising model, the plus and minus referring to the liquid and vapour phases respectively. The diameter $\rho_D = (\rho_+ + \rho_-)/2$ is

$$\rho_D = \tfrac{1}{2}(1 + \exp(-z\epsilon'/2T)). \tag{9}$$

This exact result in dimension $d > 1$ is an analytic function of T. As a particular case, the two-dimensional ($z = 4$) model is given in figure 1 since an exact solution has been given by Yang (1952) for the spontaneous magnetisation.

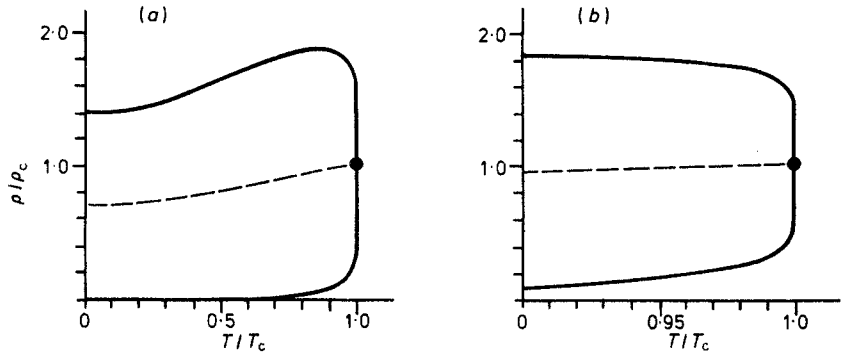

Figure 1. Liquid–vapour coexistence boundary (full curves) in the density–temperature plane for $d = 2$, $z = 4$, $\mu_0 = 0$. The broken curve is the diameter. The entire range $0 < T < T_c$ is shown in (*a*) while the region near the critical point $0{\cdot}9\,T_c < T < T_c$ is shown in (*b*). $T_c = 2\epsilon/|\ln(\sqrt{2}-1)|$, $\rho_c = 1/\sqrt{2}$.

In summary, we have presented an exactly solvable model for the liquid–vapour transition which lacks particle–hole symmetry yet has an analytic diameter. The interaction was constructed in close analogy to the WR model but our model does not show the $(T_c - T)^{1-\alpha}$ dependence of the diameter. Also it does not have many-body forces and cannot be derived from an equivalent mixture in which an effective attraction between atoms is caused by their repulsion from a different kind of atom. This type of interaction is also possible on a lattice but leads to a much more complicated Hamiltonian containing three- and four-body forces even in the simplest case (when the radius of the spheres barely exceeds the lattice spacing). The crucial difference between the WR model and ours is that the overlap volume between neighbouring spheres does not contain any lattice points and the phase transition is not equivalent to a demixing transition of a two-fluid system. On the other hand the existence of the singularity in the WR model was deduced from symmetry arguments based on the underlying demixing transition. In such a transition, when one plots the density of one component, it *is* expected that the diameter has a singularity of the $(T_c - T)^{1-\alpha}$ type.

Mermin (1971a) has proposed a 'bar' model with four-body interactions and a decorated lattice gas (Mermin 1971b), both without particle–hole symmetry and having $d\rho_D/dT \sim \ln|T_c - T|$ in two dimensions. Also in these cases the interactions between particles can be represented in terms of a two-fluid model. Other models are discussed by Rehr (1972).

However, in simple fluids, interacting via binary forces, it follows from the renormalisation group calculations (Vause and Sak 1980a, b) that the temperature dependence of ρ_D is singular, but with the exponent $\beta_5 = 1 + \frac{5}{6}\epsilon + O(\epsilon^2)$ which is related to the

anomalous dimension of the fifth power of the order parameter and is not related to α. We do not know the value of β_5 for the Ising model in dimension 2 but it could be that corrections to scaling are all analytic or absent in this case.

This work was supported by NSF grant no. DMR 79–21360 and MRL program no. 522503.

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