## Liquid-vapour critical point behaviour: especially crossover from two to three dimensions via a magnetic analogy

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# LETTER

## Liquid–vapour critical point behaviour: especially crossover from two to three dimensions via a magnetic analogy

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Motivation for this Letter comes from two experiments. The first, by Kim and Chan (Phys. Rev. Lett. **53**, 170 (1984)), measured a two-dimensional (2D) liquid–vapour critical point exponent. The second studied, via the magnetism of ultrathin metal films, the crossover of the critical exponent $\beta$ from 2D to 3D. Here, the analogy between magnetic behaviour near criticality and the corresponding liquid–vapour behaviour is first used to discuss the 2D–3D crossover in the latter case. Finally, the experimentally observed magnetic behaviour near criticality is considered for the ferromagnet $CrBr_3$ to allow fingerprints of the 3D Ising Hamiltonian to be anticipated.

**Keywords:** critical-point effects; critical exponents; crossover; Ising model; criticality; magnetic equation of state

Kim and Chan [1], a quarter of a century ago, reported the experimental determination of a two-dimensional (2D) liquid–vapour critical point (CP) exponent. Specifically, these authors mapped out the liquid–vapour coexistence boundary of submonolayer $CH_4$ adsorbed on graphite, in an extensive ac heat–capacity study. The order–parameter exponent $\beta$ that characterises the shape of the liquid–vapour coexistence boundary was thereby obtained from such measurements as $0.127 \pm 0.020$. This has prompted us to construct Figure 1 from the critical exponents known from the solution of the 2D Ising model by Onsager [2] and Yang [3] and also using the prediction $\beta = 3/8$ for 3Ds made by Zhang [4], see also [5]. We have added in Figure 1 the mean field value $\beta = 1/2$ for dimensionality $d = 4$ and $\beta = 0$ for $d = 1$. The curve shown is intended as a guide to the eye. The experimental result above [1] is in excellent agreement with Yang's 2D Ising model result $\beta = 1/8$ [3].

The remainder of this Letter is concerned with exploiting the liquid–vapour CP analogy with magnetic critical behaviour emphasised, for example, in the book by Stanley [6], to discuss the crossover behaviour from 2D to 3D. The assumed universality of CP behaviour allows magnetic behaviour at criticality to be brought into direct correspondence with that at the liquid–vapour CP. Here, we focus a good deal on experimental studies near criticality of liquid–vapour CP in 2D [1] and magnetic measurements both on

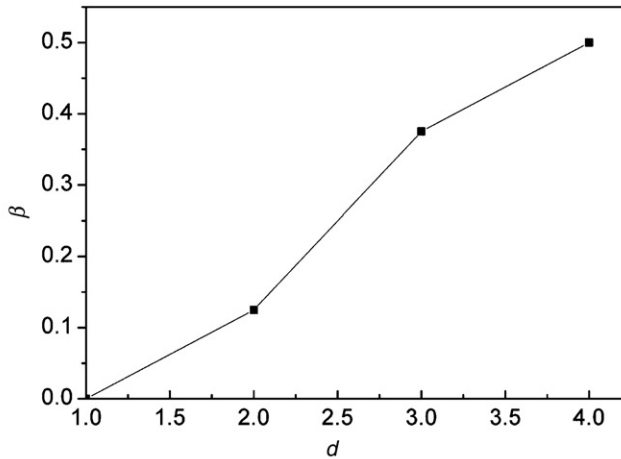*Corresponding author. Email: zdzhang@imr.ac.cn

Figure 1. Critical exponent $\beta$ as a function of dimensionality $d$, constructed from the solution of the 2D Ising model [3] and the prediction $\beta = 3/8$ for 3D made by Zhang [4], the mean field value $\beta = 1/2$ for $d = 4$ and $\beta = 0$ for $d = 1$. The curve is plotted as a guide to the eye.

the 3D insulating ferromagnet $CrBr_3$ [7,8] and on the ultrathin magnetic layers yielding the crossover behaviour from 2D to 3D of the critical exponent $\beta$ [9]. The analogue between liquid–vapour and magnetic critical behaviour allows the prediction of $\beta(d)$ in the crossover region between 2D and 3D for the liquid–vapour CP. Also, the measured magnetic equation of state near criticality allows the prediction of theoretical results expected to stem from the 3D Ising Hamiltonian.

In a magnetic system, consistent with Griffiths analyticity requirements, one can parameterise the equation of state near criticality [7]. For the insulating ferromagnet $CrBr_3$, the experimental data of Ho and Litster [8] for the magnetisation is well fitted by $m(\theta)$ as a linear function of $\theta$. The critical exponents $\beta = 0.368$, $\gamma = 1.215$ and $\delta = 4.3$, given by Schofield *et al.* [7] and Ho and Litster [8], are very close to the recent 3D Ising results given by Zhang [4], namely $\beta = 3/8$, $\gamma = 5/4$ and $\delta = 13/3$. We therefore predicted in [10] that $m(\theta)$ will be proportional to $\theta$ as a fingerprint of the 3D Ising Hamiltonian. However, before pursuing this further, let us return to the crossover between 2D and 3D behaviour, with particular reference to the 2D behaviour found experimentally by Kim and Chan [1]. Their work motivates us to discuss the 2D–3D crossover behaviour for the critical exponent $\beta$. To do this, we again appeal to the above-mentioned magnetic analogy.

We next therefore appeal to experimental results on the critical exponent $\beta$ for ultrathin metal films. Li and Baberschke [9] measured the critical exponent $\beta$ for Ni(111) films on a W(110) substrate. Their work demonstrated that a dimensionality crossover from 3D to 2D occurs with decreasing Ni film thickness. In Figure 2, we have redrawn the measurements showing the crossover region from 2D to 3D, together with Yang's exact solution for the 2D Ising model [3] and Zhang's recent 3D Ising result [4]. It is seen from Figure 2 that the critical exponent $\beta = 0.38$, obtained experimentally for bulk Ni [9], is very close to the Zhang's theoretical value $\beta = 3/8$ [4]. Meanwhile, Ni films $\leq 4$ layers thick show a truly 2D magnetic phase transition with $\beta = 0.13$ [9], which is very close to Yang's 1/8 [3]. With decreasing the thickness $t$ of Ni films, there is a crossover from 3D to 2D between the Yang's and Zhang's critical exponents $\beta$. Following the work of Klein and March [5], we
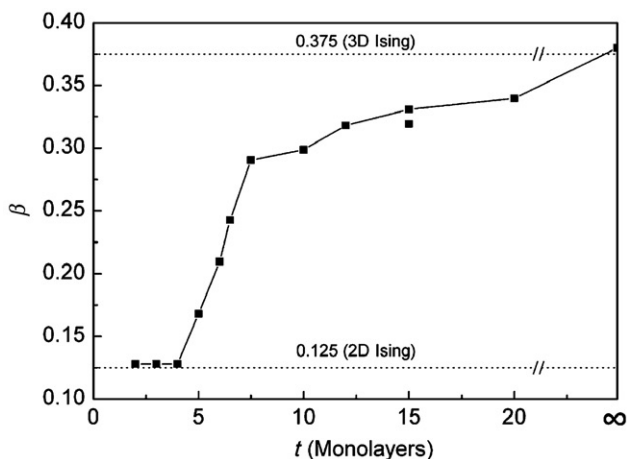
Figure 2. Critical exponent $\beta$ as a function of film thickness $t$ for Ni(111)/W(110). The experimental data are taken from Figure 2 of [9]. The dot lines show Yang's exact solution for the 2D Ising model [3] and Zhang's recent result for the 3D Ising model [4].
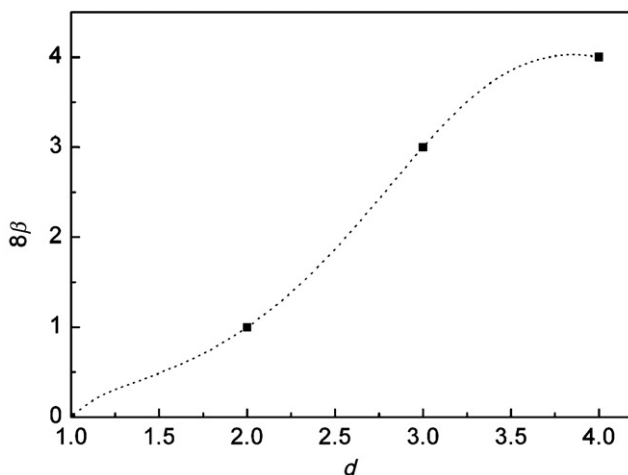


Figure 3. The $8\beta$ *vs.* $d$ curve calculated from Equations (1) and (6) of [5].

can make an interpolation via fractal dimensionality for the exponent $\beta(d)$. We plot in Figure 3 the $8\beta$ *versus* $d$ curve for the critical isotherm as a function of dimensionality $d$, which is calculated from Equations (1) and (6) of [5]. This form of $\beta(d)$ is then used in conjunction with the measurements of Li and Baberschke [9] to estimate for Ni(111) films on W(110) the relation between the dimensionality $d$ and the film thickness $t$ measured by the number of monolayers. The inverse of the thickness $t^{-1}$ *versus* $d$ curve is represented in Figure 4. It is clear that the reciprocal of the thickness $t^{-1}$ decreases first rapidly and then gradually with increasing the dimensionality $d$ from 2 to 3. In recent work [4,11] it is uncovered that the evolution of the critical behaviours in the 3D Ising lattices depends sensitively on how to change interactions along three crystallographic axes and the

symmetry of the system. In a very large district near the most symmetric (simple cubic) lattice, there is no 3D–2D crossover phenomenon [11]; but if one changes the interactions to seriously break the symmetry of the system, one will experience 3D critical behaviours, 3D–2D crossover behaviours and then 2D (and even 1D) critical behaviours in the order [11]. It is understood that the occurrence of dimensionality crossover in Ni(111) films [9] is due to the decrease of film thickness that actually introduces the asymmetry into the system.

Turning to the magnetic equation of state near criticality, Schofield *et al.* [7] utilised a parametric representation of the thermodynamic functions in the neighbourhood of the CP using variables $r$ and $\theta$. The first of these measures a 'distance' from the CP, while $\theta$ is a distance around lines of constant $r$ from one side of the coexistence curve to the other. In a magnetic system, the magnetic field $H$ can be written as the form $H = r^{\beta\delta}h(\theta)$ with the critical exponents $\beta$ and $\delta$, while the critical temperature reads $T = rt(\theta)$ and the magnetisation $M$ is given by $M = r^{\beta}m(\theta)$ [7]. For the insulating ferromagnet CrBr$_3$, the experimental results of Ho and Litster [8] is fitted with surprising accuracy by writing $m(\theta)$ as a linear function of $\theta$. Then, Schofield *et al.* [7] argued convincingly that critical exponents are related to coefficients. For CrBr$_3$, Ho and Litster gave the critical exponents as $\beta = 0.368$, $\gamma = 1.215$ and $\delta = 4.3$ [7,8]. As we stressed in [10], the very recent 3D Ising results of Zhang [4], see also [5], namely $\beta = 3/8$, $\gamma = 5/4$ and $\delta = 13/3$ are quite near to the Ho and Litster experimental findings for CrBr$_3$ [7,8]. As a consequence of this agreement, we predicted in [10] that the critical behaviour of CrBr$_3$ will be well described by the 3D Ising Hamiltonian and concluded that a fingerprint of this Hamiltonian will be that $m(\theta)$ in the formula given above for magnetisation $M$ will be proportional to $\theta$.

Our conclusions can then be summarised as follows. We have first utilised the experimental determination of a 2D liquid–vapour CP exponent by Kim and Chan [1], plus a magnetic analogy based on ultrathin magnetic layers [9] to treat the crossover of a critical exponent from 2D to 3D. Utilising the exponent $\beta(d)$ for the critical isotherm as a function of dimensionality $d$ [5], we have illustrated the relation between the dimensionality $d$ and the film thickness $t$. Exploiting further the above-mentioned magnetic analogy, we can assert
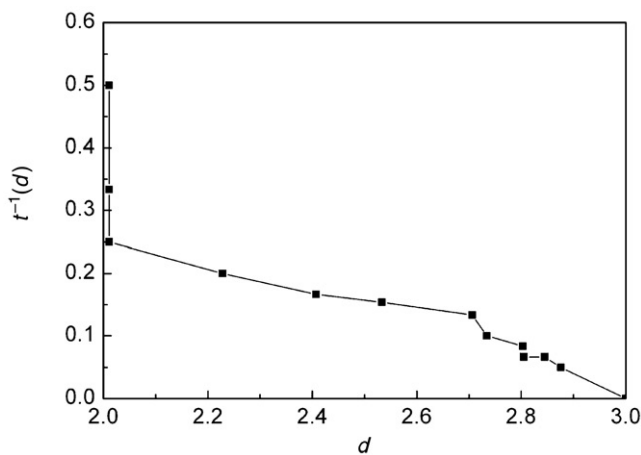


Figure 4. The inverse of the thickness $t^{-1}$ *vs.* $d$ curve obtained by utilising the experimental data in Figure 2 for film thickness dependence of the critical exponent $\beta$ and the plot in Figure 3 for the relation between the critical exponent $\beta$ and dimensionality $d$.

that, near criticality, the exponents $\beta$, $\gamma$ and $\delta$ given experimentally by Ho and Litster for CrBr$_3$ [7,8] agree to excellent accuracy with the theoretical critical exponents of Zhang [4]. The crossover critical behaviour can be observed in both the magnetic and the liquid–vapour systems as the symmetry of these systems is seriously broken down.

## Acknowledgements

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