A LETTERS JOURNAL EXPLORING THE FRONTIERS OF PHYSICS

OFFPRINT

Non-Gaussian fluctuations in monomer-dimer models

DIEGO ALBERICI, PIERLUIGI CONTUCCI and EMANUELE MINGIONE

EPL, **114** (2016) 10006

A Letters Journal Exploring the Frontiers of Physics

April 2016

EPL, **114** (2016) 10006
doi: 10.1209/0295-5075/114/10006

www.epljournal.org

Non-Gaussian fluctuations in monomer-dimer models

Diego Alberici, Pierluigi Contucci and Emanuele Mingione

Università di Bologna - Piazza di Porta San Donato 5, 40127 Bologna, Italy

received 20 January 2016; accepted in final form 18 April 2016
published online 29 April 2016

PACS 05.20.-y – Classical statistical mechanics
PACS 02.50.Cw – Probability theory
PACS 05.70.Jk – Critical point phenomena

Abstract – A hard-core monomer-dimer mean-field model is considered with the addition of an attraction potential between similar particles. We find that in the curve where the monomer and dimer phases coexist, the equilibrium state, due to the lack of gauge symmetry, turns out to be a superposition with unequal weights. We show, moreover, that at the critical point the number of monomers has non-Gaussian, quartic exponential, fluctuations.

Global physical observables in equilibrium statistical mechanics have, generically, Gaussian fluctuations on each ergodic component of the phase space. This important physical fact is theoretically understood on the basis of the central limit theorem stating that the sum of a large number (N) of random variables fluctuates around its mean proportionally to $\sqrt{N}$ if they are *sufficiently uncorrelated*. The interaction among particles nevertheless may cause, when the parameters are close to the critical point, the divergence of the correlation length and the emergence of different asymptotic behaviours whose type identifies the universality class of the system under consideration.

In this paper we study a monomer-dimer model where an attraction among particles is added to the standard hard-core repulsion. These models were introduced in statistical mechanics to describe the process of absorption of monoatomic or diatomic molecules in condensed-matter lattices [1]. Their interest and impact has progressively grown in parallel with the successful applications of those models in physics, like for the liquid mixtures with molecules of unequal size [2], and beyond. Their thermodynamic behaviour is indeed relevant in biology for studies on protein design [3], in computer science for the matching problem [4–6] or for the applications of statistical physics methods to the social sciences [7].

In physics the contact repulsion generated by the Pauli exclusion principle, that causes the divergence of the potential energy at short distance, is implemented through a configurational constraint called *hard-core interaction*: two or more particles cannot occupy the same site. When the energy of a two-particle system is in the binding region and their distance d is much larger than the equilibrium distance of their potential ($d \gg d_{eq}$), the hard core is the only relevant part of the interaction. Nevertheless when the distance is larger but close to the equilibrium one also the attractive component of the van der Waals potential has to be taken into account among monomers [8,9] and among dimers [10–13]. As already pointed out by Peierls [9], the attractive potential may induce a phase transition in the absorption process that cannot be explained with the hard-core interaction alone.

The effect of an *attractive potential* can be embedded into a pure monomer-dimer model by assigning a higher probability to those configurations that have neighbouring sites occupied by similar molecules, either both dimers or both monomers. This is the same modelling mechanism which is used in spin systems with ferromagnetic interactions where configurations with neighbouring aligned spins are favoured with respect to those with opposite alignments.

Here we focus on a monomer-dimer model with attraction among similar particles in the mean-field setting, *i.e.* on the complete graph where every site interacts with any other. In particular we investigate how the two phases (monomeric and dimeric) coexist along the critical line and how the number of monomers (or dimers) fluctuates around its mean value found in the exact solution [14,15]. The analogue problem for the mean-field ferromagnet was investigated by Ellis and Newman in [16]. Building on the exact formula for the free energy and the monomer density, we fully characterise the coexistence of phases with their relative weights in the equilibrium measure. We find, moreover, that outside the critical line the number of monomers has Gaussian fluctuations while at the critical

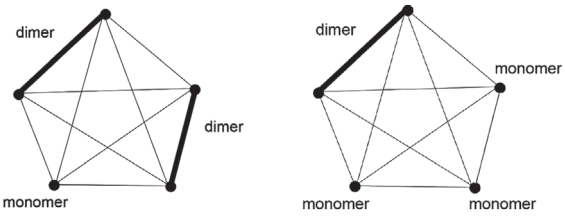

Fig. 1: Two monomer-dimer configurations on the complete graph with five sites. These configurations are allowed since each site is occupied by a single particle (*hard-core interaction*). Considering also the attractive part of the potential, the Hamiltonian of the system takes the value $-h-4J$ at the first configuration, which is made up of one monomer and two neighbouring dimers, while it takes the value $-3h-3J$ at the second one, which is made up of one dimer and three neighbouring monomers.

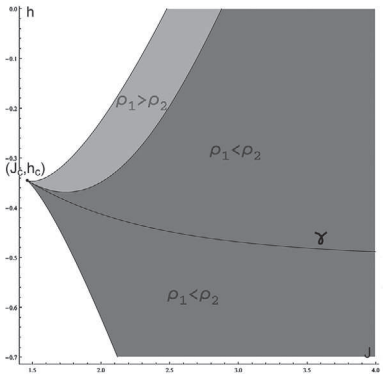

Fig. 2: The critical point (h_c, J_c) and the coexistence curve γ. The coexistence curve is completely contained in the region $\rho_1 < \rho_2$.

point the fluctuations follow an anomalous regime that scales like $N^{3/4}$ and converge, in the thermodynamic limit, toward a quartic exponential distribution. The mathematical details and proofs can be found in [17]; see also [18] for slightly extended results.

A monomer-dimer configuration D on a regular graph G with N vertices is a way to fully cover its edges by dimers and its vertices by monomers avoiding overlaps among them (hard-core interaction). We introduce a parameter $h \in \mathbb{R}$ representing the *monomer field*. Moreover, we take into account an attractive potential by introducing a *coupling* $J > 0$ among similar particles. Precisely we consider the following Hamiltonian:

$$H_N(D) = -h\, M_N(D) - J\, I_N(D), \tag{1}$$

where, for a given monomer-dimer configuration D, $M_N(D)$ is the number of monomers and $I_N(D)$ is the number of neighbouring sites occupied by the same particle kind, either both monomers or both dimers (see fig. 1).

In the present paper we consider the model on the complete graph where the correct normalisation factors that ensure a well-defined thermodynamic limit (see [19]) are given by $h + \frac{1}{2}\log N$ and J/N. The Hamiltonian (1), with the previous normalizations, induces a Gibbs probability measure on the monomer-dimer configurations given by

$$\mu_N(D) = \frac{1}{Z_N}\, \exp(-H_N(D)), \tag{2}$$

where Z_N is the partition function. We want to describe the limiting behaviour of the number of monomers M_N, under the Gibbs measure (2).

Let us start by recalling some preliminary facts from [14,15]. The pressure of the model (free energy up to a sign and a scaling factor) in the thermodynamic limit exists and is obtained as the solution of the following variational problem:

$$p = \lim_{N\to\infty} \frac{1}{N} \log Z_N = \sup_{m\in[0,1]} \tilde{p}(m), \tag{3}$$

where $\tilde{p}$ is given by

$$\tilde{p}(m) = -J\, m^2 + p^{\mathrm{MD}}((2\,m-1)J + h), \tag{4}$$

and p^{MD} is the pure hard-core monomer-dimer pressure, *i.e.* the limiting pressure at $J = 0$ and has the following expression [14,19]:

$$p^{\mathrm{MD}}(\xi) = -\frac{1}{2}(1 - g(\xi)) - \frac{1}{2}\log(1 - g(\xi)) \tag{5}$$

with $g(\xi) = \frac{1}{2}(\sqrt{e^{4\xi} + 4e^{2\xi}} - e^{2\xi})$.

The value m^* which solves the variational problem in (3) satisfies the fixed-point equation

$$m = g((2m-1)J + h). \tag{6}$$

It was proved in [14,15] that m^* represents the monomer density and is a smooth function for all the values of the parameters (h, J) with the exception of the coexistence curve γ (see fig. 2). γ is a differentiable curve in the plane (h, J) stemming from the critical point

$$(h_c, J_c) = \left(\frac{1}{2}\,\log(2\sqrt{2}-2) - \frac{1}{4},\, \frac{1}{4\,(3-2\sqrt{2})}\right). \tag{7}$$

The monomer density, moreover, is continuous but not differentiable at the critical point, while it has a jump discontinuity along the rest of the curve γ. Near the critical point it has the standard ferromagnetic mean-field exponents $\beta = 1/2$ and $\delta = 3$ [14,15].

Let us consider the number of monomers M_N as a random variable with respect to the Gibbs measure (2).

In the uniqueness region, *i.e.* outside the coexistence curve γ, the monomer density $m_N = M_N/N$ is self-averaging in the thermodynamic limit and converges in distribution to a Dirac delta at the solution of eq. (6) maximizing $\tilde{p}$:

$$m_N \xrightarrow{\mathcal{D}} \delta_{m^*}. \tag{8}$$

On the coexistence curve γ instead, there are two different solutions m_1 and m_2 of eq. (6) maximizing $\tilde{p}$ and they

represent, respectively, the *dimer* and the *monomer phase* of the system. The monomer density is distributed as a convex combination of two Dirac deltas:

$$m_N \xrightarrow{\mathcal{D}} \rho_1\,\delta_{m_1} + \rho_2\,\delta_{m_2}, \tag{9}$$

where $\rho_l = \frac{b_l}{b_1+b_2}$, $l = 1, 2$, $b_l = (-\lambda_l(2-m_l))^{-1/2}$ and $\lambda_l = \frac{\partial^2}{\partial m^2}\widetilde{p}(m_l)$.

We notice that the Hamiltonian (1) is formally similar to the Hamiltonian of a mean-field ferromagnet; however, there are two main differences between these models: in the monomer-dimer model the configuration space is not a product space because of the hard-core constraint, moreover there is not a gauge symmetry (like the spin flip). One can appreciate the effects of these differences on the phase transition of the model by observing the statistical weights ρ_1, ρ_2. Indeed, in the mean-field ferromagnet, because of the presence of the spin-flip symmetry, the statistical weights of the two phases on the coexistence curve (zero external field) are both equal to $1/2$, for any value of the coupling above the critical one. Conversely, for the monomer-dimer model, the statistical weights ρ_1 and ρ_2 are in general different (see fig. 2). Moreover, unlike in the ferromagnetic case, $\rho_{1,2}$ depends also on the extra factor $(2-m_l)^{-1/2}$ that can be related (see [20]) to the presence of the hard-core interaction.

Monomer-dimer models without the attractive component of the interaction ($J = 0$) have been proved, by Heilmann and Lieb [19,21], to have analytic thermodynamic functions and, as a consequence, their fluctuations are normal [22]. In our case instead the presence of the attractive component of the interaction makes the problem highly non-trivial.

Outside the critical curve γ the number of monomers M_N has normal fluctuations around its mean:

$$\frac{M_N - Nm^*}{N^{1/2}} \xrightarrow{\mathcal{D}} \frac{1}{\sqrt{2\pi\sigma^2}}\, e^{-\frac{x^2}{2\sigma^2}}, \tag{10}$$

where $\sigma^2 = -\lambda^{-1} - (2J)^{-1} > 0$ and $\lambda = \frac{\partial^2}{\partial m^2}\widetilde{p}(m^*) < 0$. At the critical point instead the second derivative of the pressure vanishes and the Gaussian regime for the fluctuations does not hold any more. The fluctuations of the number of monomers are not of order $\sqrt{N}$ but larger, *i.e.* $N^{3/4}$. The limiting distribution turns out to be a quartic exponential:

$$\frac{M_N - Nm_c}{N^{3/4}} \xrightarrow{\mathcal{D}} \frac{\sqrt[4]{\lambda_c}}{2\sqrt[4]{24}\,\Gamma(\frac{5}{4})}\, e^{-\frac{\lambda_c x^4}{24}}, \tag{11}$$

where $\lambda_c = -\frac{\partial^4}{\partial m^4}\widetilde{p}(m_c) > 0$, $m_c = m^*(h_c, J_c)$.

We have shown that the addition of an attractive potential in the interaction of a mean-field monomer-dimer system leads to a critical point with non-Gaussian fluctuations. It would be interesting to extend the present result to the random-graph case studied in [23,24] or to add a random monomer activity as in [20,25].

The present result is intended as a first step toward the study of monomer-dimer systems in finite dimensions, especially $d = 2, 3$. There are indeed experimental results displaying non-Gaussian fluctuations, like, for instance, those for liquid crystals presented in [26] that have been theoretically understood as induced by finite-size effects. It would be interesting to investigate whether similar structures at the critical point could also be found with mathematically rigorous approaches.

REFERENCES

[1] Roberts J. K., *Proc. Cambridge Philos. Soc.*, **34** (1938) 399.

[2] Fowler R. H. and Rushbrooke G. S., *Trans. Faraday Soc.*, **33** (1937) 1272.

[3] O'Neil K. T. and DeGrado W. F., *Science*, **250** (1990) 646.

[4] Karp R. and Sipser M., *Maximum matchings in sparse random graphs*, in *Proceedings of the 2nd Annual Symposium on Foundations of Computer Science* (IEEE Computer Society Press) 1981, pp. 364–375.

[5] Zdeborová L. and Mézard M., *J. Stat. Mech.* (2006) P05003.

[6] Bordenave C., Lelarge M. and Salez J., *Probab. Theory Relat. Fields*, **157** (2013) 183.

[7] Barra A., Contucci P., Sandell R. and Vernia C., *Sci. Rep.*, **4** (2014) 4174.

[8] Fowler R. H., *Math. Proc. Cambridge Philos. Soc.*, **32** (1936) 144.

[9] Peierls R., *Math. Proc. Cambridge Philos. Soc.*, **32** (1936) 471.

[10] Roberts J. K. and Miller R., *Proc. Cambridge Philos. Soc.*, **35** (1939) 293.

[11] Chang T. S., *Proc. R. Soc. London, Ser. A*, **169** (1939) 512.

[12] Chang T. S., *Proc. Cambridge Philos. Soc.*, **38** (1939) 256.

[13] Heilmann O. J. and Lieb E. H., *J. Stat. Phys.*, **20** (1979) 680.

[14] Alberici D., Contucci P. and Mingione E., *J. Math. Phys.*, **55** (2014) 063301.

[15] Alberici D., Contucci P. and Mingione E., *EPL*, **106** (2014) 10001.

[16] Ellis R. S. and Newman C. M., *J. Stat. Phys.*, **19** (1978) 149.

[17] Alberici D., Contucci P., Fedele M. and Mingione E., *Limit theorems for monomer-dimer mean-field models with attractive potential*, to be published in *Commun. Math. Phys.* (2015), doi 10.1007/s00220-015-2543-1.

[18] Chen W. K., *Limit Theorems in the imitative monomer-dimer mean-field model via Stein's method*, preprint arXiv:1506.08484 (2015).

[19] Heilmann O. J. and Lieb E. H., *Commun. Math. Phys.*, **25** (1972) 190.

[20] Alberici D., Contucci P. and Mingione E., *J. Stat. Phys.*, **160** (2015) 1721.

[21] Heilmann O. J. and Lieb E. H., *Phys. Rev. Lett.*, **24** (1970) 1412.

[22] Lebowitz J. L., Pittel B., Ruelle D. and Speer E. R., *Central limit theorems, Lee-Yang zeros, and*

graph-counting polynomials, preprint arXiv:1408.4153 (2014).

[23] Alberici D. and Contucci P., *Commun. Math. Phys.*, **331** (2014) 975.

[24] Dommers S., Giardina C., Giberti C., van der Hofstad R. and Prioriello M. L., *Ising critical behavior of inhomogeneous Curie-Weiss and annealed random graphs*, preprint arXiv:1509.07327.

[25] Amaro de Matos J. M. G. and Fernando Perez J., *J. Stat. Phys.*, **62** (1991) 587.

[26] Joubaud S., Petrosyan A., Ciliberto S. and Garnier N. B., *Phys. Rev. Lett.*, **100** (2008) 180601.