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Phase transitions driven by competing interactions in low-dimensional systems

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Abstract – Variable-temperature scanning tunnelling microscopy is used to study an order-order phase transition in a virtually defect-free quasi-one-dimensional surface system. The phase transition is driven by competing electronic interactions. The phase diagram is captured by a modified Landau formalism containing a coupling term between two different subsystems. The extra term has the effect of a spontaneously generated field which drives the phase transition. The proposed formalism applies to a variety of problems, where competing interactions produce sometimes counter-intuitive ordering phenomena.

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In Landau theory [1] first-order phase transitions are typically described by an expansion of the free energy in terms of the order parameter m up to the 6th order. For a qualitative description of continuous phase transitions, in contrast, the expansion can be truncated after the fourth-order term. Introduction of an external field which couples to the order parameter results in a linear term in the expansion and converts a continuous into a first-order phase transition. Here we present a study of phase transitions occurring in a quasi-one-dimensional (quasi-1D) surface system. The phase transition has highly anomalous features, such as quasi-critical fluctuations occurring over a wide temperature range. The experimental phase diagram can be reproduced by inserting a linear term into a fourth-order Landau expansion. The additional term arises from an internal coupling between adsorbate and substrate. Interactions in each of the subsystems compete with one another. Since their temperature dependence is different, a phase transition occurs as a function of temperature. The coupling between the subsystems has the effect of a spontaneously generated field which drives a weakly first-order phase transition. The proposed model is

shown to be of rather general relevance. A similar coupling mechanism is at work in widely different materials such as aqueous polyelectrolyte-counterion systems and so-called composite crystal structures [2].

The quasi-1D model system used in the present study is based on the anisotropy of fcc (110) metal surfaces. The anomalous phase transition investigated here occurs on a bromine-covered Pt(110) surface with a coverage of $\Theta_{\text{Br}} = 0.5$ ML (a monolayer (ML) is defined as the atom density of the unreconstructed Pt(110)-(1 × 1) surface). At room temperature a long-range ordered, quasi-hexagonal $c(2 \times 2)$ -Br/Pt(110) phase is observed (“checkerboard phase”; fig. 1(a)) with Br atoms sitting in short-bridge sites. Upon cooling below 200 K, long-range order is destroyed and low-energy electron diffraction (LEED) as well as STM indicate the existence of rapid fluctuations [3]. At about 50 K the fluctuations become so sluggish that it is possible to obtain atomically resolved STM images. Figure 1(b) shows a large-scale image of the structure at 50 K exhibiting a conspicuous pattern of dark and bright stripes. The bright stripes are $c(2 \times 2)$ (checkerboard) domains as before, while in the dark stripes the Br atoms are arranged in a (2×1) pattern, henceforth to be called “rectangular phase” (fig. 1(d)). The domain pattern appears to

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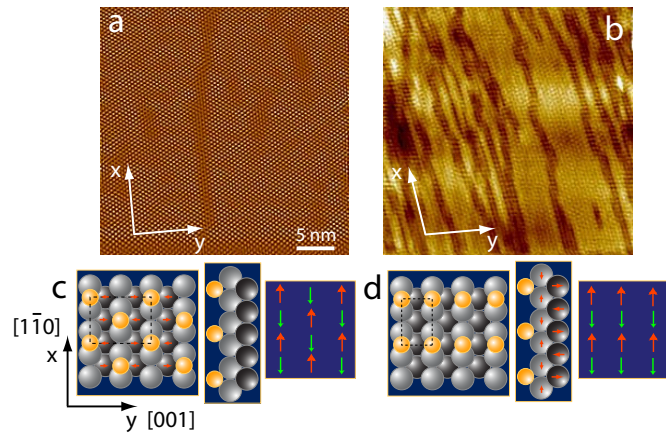


Fig. 1: Variable-temperature STM images of 0.5 ML Br on Pt(110) and corresponding structure models. (a) Point-defect-free $c(2 \times 2)$ (checkerboard) structure observed at 300 K. The slightly darker vertical strip in the left half of the image is a domain boundary between two phase-shifted $c(2 \times 2)$ domains. (b) 1D pattern obtained after cooling the same preparation to 50 K. The bright domains correspond to a local $c(2 \times 2)$ (checkerboard) order, the dark stripes to a (2×1) (rectangular) structure. Due to thermal drift the image is slightly distorted. (c) Ball model of the $c(2 \times 2)$ structure, showing the view from the top and cut through the surface parallel to the close-packed row direction of the Pt substrate. Light- and dark-gray balls correspond to first- and second-layer substrate atoms, respectively, while yellow balls designate adsorbed Br atoms. Red arrows indicate a slight pairing of substrate atoms. (d) Ball model of the (2×1) structure. Note the pronounced buckling indicated by the red arrows in the second layer of the Pt substrate. Panels (c) and (d) show a pseudo-spin representation of the respective structures as explained in the text.

be self-affine with respect to rescaling in the y -direction (*i.e.* no preferred length scale within the window of observation). The meandering of the domain boundaries indicates a vanishing domain boundary energy. The structure shown in fig. 1(b) is characteristic of a critically fluctuating quasi-1D system (to our knowledge this is the first snapshot of such fluctuations in a quasi-1D system; cf. 2D critical fluctuations shown in ref. [4]). However, an upper cut-off length may appear on a larger scale. Density functional theory (DFT) calculations place the rectangular structure 20 meV/Br atom below the checkerboard phase identifying the former as the true ground state at 0 K. Note that the accuracy of the DFT calculations for the present system has been extensively tested with respect to energetic and geometric structure [5–7], hence there is little doubt about the stability of the rectangular structure. In contrast to previously analysed order-order transitions in adsorbate systems [8], the entropy in the adsorbate layer cannot be the driving force in the present case, because the local adsorbate site stays the same. The small change in free volume associated with the $(2 \times 1) \rightarrow c(2 \times 2)$ transition yields only a negligible entropy contribution. While the quasi-hexagonal

checkerboard structure is favoured by the Br-Br repulsion, the low-temperature (2×1) phase is apparently stabilised by the substrate. The rectangular structure is indeed associated with a considerable periodic lattice distortion down to the third layer of the substrate. Although the precise nature of the substrate-induced stabilisation mechanism is not essential for the following discussion, circumstantial evidence strongly suggests the formation of a charge density wave (CDW) with a concomitant periodic lattice distortion [6,7,9,10]. This explanation is supported by the observation of a strong Kohn anomaly in the Pt bulk revealing an inherent instability of Pt towards a Peierls distortion [11]. The phase transition can thus be understood in terms of the competition between the Br-Br repulsion and the Peierls interaction. The CDW forming below the Peierls temperature T_c^P rearranges the Br layer into the rectangular structure. The coupling of the Br atoms to the CDW fluctuations stabilises the Peierls phase in a kind of bootstrap mechanism. Formation of a CDW with periodicity of two lattice constants requires a maximum in the electronic response function $\chi(q)$ of the substrate at $q = 1/2G$, where G is a reciprocal lattice vector [12]. Angle-resolved UV photoemission indicates that this is actually the case in the present system [13], but the universal physics of the phase transition we shall discuss in the following does not depend on the details of the electronic mechanism which stabilises the ground state. Any substrate-mediated interaction which at low temperature overtakes the inter-adsorbate repulsion will have the same effect. However, for simplicity we refer to the Peierls mechanism hereafter.

Introducing a (classical) Ising pseudo-spin $s = \pm 1/2$ for occupied and unoccupied short-bridge sites, respectively, the inter-adsorbate repulsion is represented by effective exchange couplings J_{\parallel} , J_{\perp} , where parallel and perpendicular refers to the close-packed row direction. DFT calculations show that $J_{\parallel} > J_{\perp}$. Thus in a first approximation the inter-adsorbate distance is considered to be fixed along the rows and the relevant degree of freedom is a rigid shift of neighbouring rows relative to each other. Within this approximation, the problem is reduced to one dimension. The free-energy functional contains the adsorbate-adsorbate repulsion across the rows, the Landau expansion in terms of a CDW order parameter m up to the quartic term and, most significant in the present context, a coupling term between the CDW and the adsorbate with coupling strength g :

$$H/L_{\parallel} = J_{\perp} \sum_i s_i s_{i+1} + gm \sum_i s_i + \frac{L_{\perp}}{a_{\perp}} \left(\frac{\alpha}{2} m^2 + \frac{\lambda}{4} m^4 \right).$$

$H/(L_{\parallel}L_{\perp})$ is the free-energy density of the quasi-1D system. The coupling term of the CDW order parameter to the pseudo-spins has the form of an external field which, being spontaneously generated (see below), drives the phase transition. The temperature dependence of the CDW order is represented by the standard choice of

coefficients $\alpha = \alpha_0(T - T_c^P)$ and $\lambda = \text{const}$ [14]. i is the index counting the rows, L_\perp and L_\parallel are the sample dimensions, a_\perp is the row-to-row distance. Of course, in a 2D or 1D system no real long-range order would develop at finite temperature [15], but a quasi-long-range order with a correlation length comparable to the terrace dimensions L_\parallel , L_\perp is sufficient to justify the use of a global order parameter in the present context.

In the checkerboard phase $s_i = -s_{i+1}$, hence the coupling to m vanishes, the energy density E_{cb} is minimized for $m = 0$ and $E_{cb} = -\frac{1}{4}J_\perp/a_\perp$ (note that $\sum_i s_i s_{i+1} = -\frac{1}{4}L_\perp/a_\perp$). In the rectangular phase we have $s_i = s_{i+1}$. We define $g > 0$ without loss of generality and therefore the minimum of the energy density E_{rect} occurs for $s_i = -1/2$. The physically relevant regime here is the one close to spontaneous CDW formation, *i.e.* $\alpha \rightarrow 0$. By minimising the free energy with respect to the order parameter m in the usual way and expanding in powers of α , the expectation value $\langle m \rangle$ is obtained to leading order in α as

$$\langle m \rangle = \left(\frac{g}{2\lambda} \right)^{1/3} \left(1 - \frac{\alpha}{3(\frac{\lambda g^2}{4})^{1/3}} \right).$$

This is valid, as long as $\alpha \ll 3(\lambda g^2/4)^{1/3}$, *i.e.* close to the transition temperature T_c^P . In this temperature range, the energy density of the rectangular phase is then

$$E_{rect} \approx \frac{1}{4a_\perp} \left(J_\perp - \frac{3}{2}g \left(\frac{g}{2\lambda} \right)^{1/3} \right),$$

yielding a critical point at $3g(g/2\lambda)^{1/3} \approx J_\perp$. The parameter J_\perp as well as the stability of the Peierls phase depend on $r_\perp = a_\perp/r_{aa}$, where r_{aa} is the characteristic range of the repulsive adsorbate-adsorbate potential across the troughs. In the present case the repulsion is neither the Pauli repulsion of overlapping adsorbate electron densities nor electrostatic in nature. Rather it is a substrate-mediated RKKY-type interaction. This conclusion arises from the strong anisotropy of the repulsive potential and its adsorption-site-dependent range [7]. J_\perp scales with $r_\perp^{-5/2}$ on the surface of a semi-infinite metal [16] and with r_\perp^{-2} , if the interaction is mediated by a 2D surface state [17]. The dependence of the Peierls phase stability on r_\perp is intricate: large r_\perp implies a weak coupling between the close-packed atom rows. Hence, the Fermi surface is more anisotropic, approaching with increasing r_\perp the ideal 1D case, *i.e.* increasingly perfect nesting. In summary, for $r_\perp \rightarrow 0$ the Br-Br repulsion J_\perp is dominant and stabilises the checkerboard structure up to a disordering temperature of $T_c^d = 2.28 J_\perp/k_B$. For large r_\perp , J_\perp and therefore T_c^d goes down, whereas the increasing anisotropy of the system favours the CDW phase and T_c^P goes up. A sketch of the resulting phase diagram is given in fig. 2. Note that for $r_\perp \rightarrow \infty$ the 2D order breaks down and the physics changes altogether [18]. If Br is replaced by Cl as an adsorbate, r_{aa} is smaller and r_\perp increases.

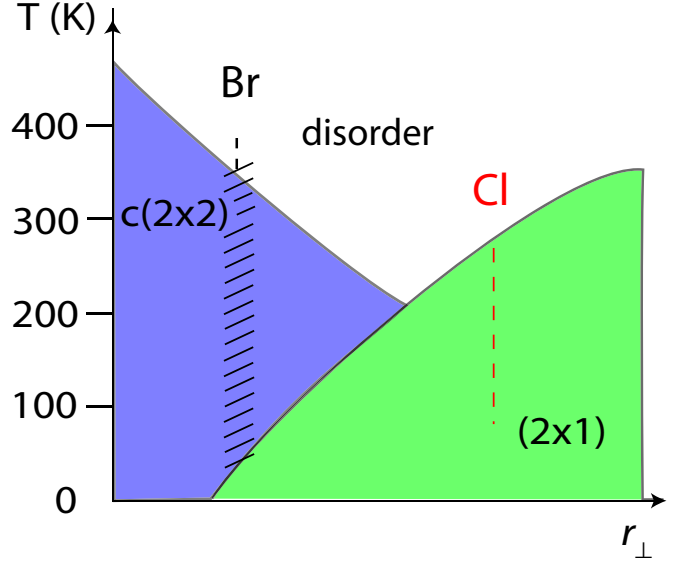


Fig. 2: Schematic phase diagram based on a competition between adsorbate-adsorbate repulsion and Peierls interaction. The phase transition results from the competition between the “Ising coupling” J_\perp describing the repulsive interaction of the ad-atoms and the coupling g of the overlayer atoms to the charge density wave (CDW). As the parameter r_\perp is increased, the ordering temperature for the checkerboard structure drops, while the rectangular (CDW) phase is stabilised with increasing 1D character. The hatched area along the “Br-trajectory” indicates the range, where intense fluctuations are observed.

Consequently, for Cl the rectangular phase is stable up to room temperature [19].

Despite the phase transition being first-order, intense fluctuations are observed over a large temperature range. Hence a term $\kappa^2(\nabla m(x))^2$ has to be added to the free-energy functional accounting for spatial variations of the order parameter. According to the Ginzburg-Levanjuk criterion, derived for the original Landau expansion, fluctuations become negligible only for

$$1 \gg \frac{\lambda k_B T_c}{2\kappa^4} \left(\frac{2\kappa^2}{\alpha_0 |T - T_c|} \right)^{\frac{4-d}{2}}$$

with d being the dimensionality of the system. The criterion remains valid even in the present case where the coupling to the adsorbate system is included. The criterion is derived from a calculation of the free-energy fluctuations $\Delta F \approx 1/2(m - \bar{m})^2 \partial^2 F / \partial m^2|_{m=\bar{m}}$. Clearly, the first two terms in the present model which describe the inter-adsorbate repulsion and the coupling of the adsorbate to the substrate order parameter do not enter this expression. For $d = 2$ the temperature range of fluctuations is estimated as $\tau \approx \lambda k_B / \kappa^2 \alpha_0$, where $\tau = (T - T_c) / T_c$. The temperature range scales inversely with the product $\kappa^2 \alpha_0$, *i.e.* it can be large, provided α_0 and the domain wall energy is small. The latter is indicated by the meandering of the domain walls visible in fig. 1. For $d < 2$ the criterion

is even more relaxed. Thus, the anomalously extended fluctuation regime results essentially from the low dimensionality of the system. Within this regime, Landau theory is not strictly applicable. The above discussion should therefore be viewed as a qualitative analysis of the interactions determining the phase diagram, but does not allow for a quantitative description.

The modified Landau theory presented here is a 1D approximation designed to explore the essential consequences of the adsorbate-substrate coupling in a most transparent way. This works, because the surface system is extremely anisotropic as, *e.g.*, indicated by the domain structure in fig. 1(b). A more precise description requires a full 2D version of the same type, including both, the Br-Br repulsion along the rows and the free energy of domain boundaries perpendicular to the rows. Without these terms the weak, but significant meandering of the stripes seen in fig. 1(b) cannot be captured. In fact, the fluctuations which convert the checkerboard domains into rectangular structure and vice versa even at 50 K are caused by the mobility of [001] domain boundaries in the direction along the close-packed rows. A discussion of the full 2D extension of the present model and the atomic processes causing the domain boundary fluctuations is however beyond the scope of the present paper.

The adsorbate-substrate coupling acts like a spontaneously generated external field: its presence stabilises at low temperature the rectangular phase in a bootstrap mechanism and renders the transition weakly first order. Such a coupling between two different subsystems with competing interactions occurs in widely different systems. The coupling of quasi-1D structural motives has recently been analysed in a beautiful study of aqueous polyelectrolytes [20]. Specifically, the condensation of F-actin filaments around 1D counterion strings has been investigated. Contrary to naive expectation the counterion charge density is not uniformly smeared, but a pronounced charge density modulation is observed. In response to this modulation, or actually in a mechanism of mutual stabilisation, the F-actin strands adopt a new twisting periodicity changing from a 13/6 helix to a 36/17 helix. The latter reduces the electrostatic and steric defect interaction energy of the three filament bundles formed around the 1D counterion strand at the expense of elastic deformation energy. Without the CDW response of the counterions this configuration is unstable. Since, however, the counterions lock into the new periodicity, the 36/17 configuration emerges as the ground state. In terms of the free-energy expansion discussed here, it is precisely the coupling between the 36/17 order parameter and the counterion charge density, which stabilises the configuration.

We propose that a similar concept also applies for composite crystal structures, *i.e.* “structures that have two or more mutually interpenetrating substructures with incommensurate or commensurate periods along some (one or two) directions. Each substructure is modulated

by the interaction with the others” [2]. Quasi-1D examples include K_2SeO_4 [21,22], $(\text{TTF})_7\text{I}_{5-x}$ and $\text{Hg}_{3-\delta}\text{AsF}_6$ [23]. Note that the actual superstructure is not just the coincidence structure of the two subsystems (*i.e.* a Moiré-type structure). Rather, both subsystems adopt the *same* (in)commensurate superstructure periodicity. In the examples mentioned the second subsystem consists simply of identical counterions. Evidently, the counterion subsystem does not have a preferred periodicity of its own. Minimisation of the electrostatic energy would require a uniform, maximum distance between the counterions. Periodic density variations or sinusoidal site modulations arise obviously from the coupling to the primary subsystem. The primary system, in turn, would have a different periodicity in the absence of the counterions. Thus it is the coupling between the two subsystems, which stabilises the superstructure order parameter. The mechanism proposed here stresses the response of the counterion system to fluctuations of the order parameter in the primary system. The coupling lowers the free energy of an otherwise unstable or metastable configuration, eventually rendering it the new groundstate. According to the schematic phase diagram (fig. 2), the number of phase transitions observed in the system may change with the coupling strength.

For quasi-1D systems, we expect a strong tendency to develop fluctuations as the phase transition is approached where the superstructure order parameter disappears. For instance, $\text{Hg}_{3-\delta}\text{AsF}_6$ exhibits a disordered phase above 120 K, “indicating partial occupation by mercury of different crystallographic positions” [23]. We stress, however, that correlated fluctuations are likely in this regime. Depending on the parameters in the Ginzburg-Levanjuk criterion, the phase transition may appear as quasi-continuous due to strong fluctuations. From our point of view, the role of fluctuations has not in general been sufficiently appreciated and analysed in the quasi-1D bulk systems discussed here. Such fluctuations represent a highly interesting state of matter. For instance, critical Casimir forces [24] are a manifestation of novel interactions arising in a fluctuating medium. In fact, Casimir forces have been invoked to account for counter-ion mediated attractions in polyelectrolytes [25]. In contrast to 2D critical fluctuations demonstrated earlier [4] to our knowledge no fluctuating quasi-1D structure has been imaged previously. The reason is the extreme sensitivity of phase transitions in quasi-1D systems against defects. Even very low defect concentrations tend to destroy the anisotropy in the correlation length and thus obscure the 1D character of the correlated fluctuations. This is exemplified by a comparison of the results reported earlier in ref. [3] with the present observations: the 1D character of the domains was less pronounced and the almost scale-free behaviour seen in fig. 1(b) was absent in the previous preparation which contained a significantly higher defect density. Most prominently, a third structural motive was found in ref. [3], namely a (3×2) structure not appearing in the present

data. The defects set a new extrinsic length scale, thus obscuring the differences between parallel and perpendicular coherence lengths in quasi-1D systems. The scale-free behaviour, a fingerprint of quasi-critical fluctuations characteristic for low-D systems, is suppressed by the defects, since they pin the domain boundaries. Last, but not least, the appearance of a third structural motive signals that the presence of defects prevents even for $T \rightarrow 0$ K the evolution of the system into the global groundstate as will be discussed elsewhere.

In summary, we propose a modified Landau theory of phase transitions which incorporates a coupling between subsystems with competing interactions. The coupling works as an effective external field triggering a phase transition in a kind of bootstrap mechanism. The model describes well the phase diagram reported here for a quasi-1D surface system, but has wider implications for a variety of materials with coupled low-D subsystems.

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REFERENCES

- [1] BINDER K., in *Phase Transformations in Materials*, edited by KOSTORZ G. (Wiley-VCH, Weinheim) 2001, p. 239.
- [2] YAMAMOTO A., *Acta Crystallogr. A*, **49** (1993) 831.
- [3] DONÁ E., LOERTING T., PENNER S., MINCA M., MENZEL A., BERTEL E., SCHOISWOHL J., BERKEBILE S., NETZER F. P., ZUCCA R. and REDINGER J., *Phys. Rev. Lett.*, **98** (2007) 186101.
- [4] NIELSEN L. K., BJORNHOLM T. and MOURITSEN O. G., *Nature*, **404** (2000) 352.
- [5] BLUM V., HAMMER L., HEINZ K., FRANCHINI C., REDINGER J., SWAMY K., DEISL C. and BERTEL E., *Phys. Rev. B*, **65** (2002) 165408.
- [6] DEISL C., SWAMY K., MEMMEL N., BERTEL E., FRANCHINI C., SCHNEIDER G., REDINGER J., WALTER S., HAMMER L. and HEINZ K., *Phys. Rev. B*, **69** (2004) 195405.
- [7] DEISL C., DONA E., PENNER S., GABL M., BERTEL E., ZUCCA R. and REDINGER J., *J. Phys.: Condens. Matter*, **21** (2009) 134003.
- [8] GU J., SIM W. S. and KING D. A., *J. Chem. Phys.*, **107** (1997) 5613.
- [9] SWAMY K., MENZEL A., BEER R. and BERTEL E., *Phys. Rev. Lett.*, **86** (2001) 1299.
- [10] DEISL C., SWAMY K., BEER R., MENZEL A. and BERTEL E., *J. Phys.: Condens. Matter*, **14** (2002) 4199.
- [11] DUTTON D. H., BROCKHOUSE B. N. and MILLER A. P., *Can. J. Phys.*, **50** (1972) 2915.
- [12] CALANDRA M., MAZIN I. I. and MAURI F., *Phys. Rev. B*, **80** (2009) 241108.
- [13] AMANN P., CORDIN M., BRAUN C., LECHNER B. A. J., MENZEL A., BERTEL E., FRANCHINI C., ZUCCA R., REDINGER J., BARANOV M. and DIEHL S., *Eur. Phys. J. B*, **10** (2010) 15.
- [14] GRÜNER G., *Density Waves in Solids* (Perseus Publishing, Cambridge, Mass.) 1994.
- [15] MERMIN N. D. and WAGNER H., *Phys. Rev. Lett.*, **17** (1966) 1133.
- [16] LAU K. H. and KOHN W., *Surf. Sci.*, **75** (1978) 69.
- [17] HYLDGAARD P. and PERSSON M., *J. Phys.: Condens. Matter*, **12** (2000) L13.
- [18] GIAMARCHI T., *Quantum Physics in One Dimension* (Oxford University Press, New York) 2004.
- [19] DONÁ E., CORDIN M., DEISL C., BERTEL E., FRANCHINI C., ZUCCA R. and REDINGER J., *J. Am. Chem. Soc.*, **131** (2009) 2827.
- [20] ANGELINI T. E., LIANG H., WRIGGERS W. and WONG G. C. L., *Proc. Natl. Acad. Sci. U.S.A.*, **100** (2003) 8634.
- [21] YAMADA N. and IKEDA T., *J. Phys. Soc. Jpn.*, **53** (1984) 2555.
- [22] JANNER A. and JANSSEN T., *Acta Crystallogr. A*, **36** (1980) 399.
- [23] JANNER A. and JANSSEN T., *Acta Crystallogr. A*, **36** (1980) 408.
- [24] HERTLEIN C., HELDEN L., GAMBASSI A., DIETRICH S. and BECHINGER C., *Nature*, **451** (2008) 172.
- [25] GELBART W. M., BRUINSMA R. F., PINCUS P. A. and PARSEGHIAN V. A., *Phys. Today*, **53**, issue No. 9 (2000) 38.