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New physical phases induced by confinement

S Dietrich

Fachbereich Physik, Bergische Universität Wuppertal, D-42097 Wuppertal, Germany

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Abstract. The properties of fluids exposed to chemically or geometrically structured substrates are discussed. The relevance of these studies for experiments and applications is pointed out.

The traditional pathway to new physical phases is to explore new regions in the parameter space of external thermodynamic variables such as pressure, temperature, and electric or magnetic fields. Typically these explorations are either experimentally very demanding due to extreme conditions or they are only realized in outer space. This severely impedes a critical comparison between theoretical predictions and experimental data.

An alternative route to new phases is offered by the fact that structural properties of condensed matter can be varied not only by changing the external thermodynamic variables, but that they are also dependent on the spatial dimension d . The confinement of condensed matter to thin films facilitates the formation of structures which do not occur either in $d = 2$ nor in $d = 3$ space dimensions. By changing the film thickness L one can interpolate continuously between the limiting structures in $d = 2$ and $d = 3$. Imposing additional confinements in one or two lateral directions leads to a further decrease of the effective spatial dimension resulting in quasi-one-dimensional or quasi-two-dimensional structures, respectively. This allows one to explore the full spatial range $0 \leq d \leq 3$ providing a very rich variety of new phases and phase transitions which do not occur in bulk materials.

In the case of fluids the confinement can be achieved by solid inert substrate walls of suitable shape and composition. However, the precision with which a well-defined geometry can be arranged is severely limited by alignment difficulties. These problems can be overcome by exploiting wetting phenomena [1] in which a substrate is exposed to the vapour phase of a fluid such that the competition between the substrate potential and the interaction between the fluid particles brings about the formation of a liquid-like film covering the substrate and whose thickness can be adjusted systematically between atomic scales of a few Å up to mesoscopic scales reaching μm thicknesses by varying the temperature or the pressure close to liquid–vapour coexistence in the bulk. Thus the liquid-like film is confined by the fixed substrate–liquid interface on one side and the emerging liquid–vapour interface on the other side whose position can depend from the substrate. In this way a parallel plate geometry can be obtained which is technically impossible using two hard walls. An overview of the rich phase behaviour associated with these wetting phenomena can be found in [1]. A major virtue of these systems is that their structures and the phase transitions are accessible in great detail both theoretically and experimentally allowing for a fruitful interplay between both approaches. On the theoretical side density functional theory, Monte Carlo and molecular dynamics simulations, Landau theories and

field-theoretical renormalization group techniques have proven to be very successful. The loss of translational invariance, the confinement, and the competition between various interactions represent rewarding theoretical challenges. On the experimental side a wide spectrum of techniques has been developed to probe these structural properties in great detail. Among them are optical techniques like reflectometry and ellipsometry, force microscopy, and x-ray and neutron scattering. The latter technique offers the particularly powerful potential to gain access not only to the density distribution normal to the interface position but, by analyzing the diffuse scattering intensity around the specular beam of totally reflected x-rays or neutrons, also to the depth-resolved lateral structure factor [2]. This can provide a highly accurate picture of the new structures forming in the films. Third generation synchrotron sources are ideally suited to accomplish this goal.

These thin fluid films are not only of outstanding theoretical and experimental interest but in addition they offer the possibility of important applications. The already wide range of applications for homogeneous wetting films has been broadened significantly by the newly achieved possibilities to endow solid surfaces with well-defined, lateral geometrical or chemical structures. By using microcontact printing techniques a homogeneous smooth substrate can be covered by an overlayer which is firmly anchored on this substrate containing designed patterns of hydrophobic and hydrophilic areas such that the wetting film is adsorbed preferentially on distinct regions only. By using suitable components for this overlayer its smooth geometric topography can be maintained so that the fluid is exposed only to chemical steps in lateral directions. Such structures can be used, e.g., in the context of microfluidics. These chemical lanes are used as guiding systems in order to deliver tiny amounts of valuable fluids, which may for example contain rare biomaterials, to designated analysis centres on the surface. Such features can be integrated to build a chemical chip within which different kinds of fluid can be processed in small-scale chemical factories. In the same way that quantum mechanics is used to explore the lower limits of miniaturization of traditional chips due to quantum fluctuations, statistical physics can be used to explore the limits of miniaturization of chemical chips set by thermal fluctuations. The objective is, e.g., to explore to what precision liquid ridges can be kept on a chemical strip without significant spill-over to a neighbouring strip. Moreover, by using density functional theory statistical physics offers the capability to explore the functional dependence of these fluid structures on the underlying substrate potentials and interaction potentials between the fluid particles such that an optimal performance can be tailored. These chemical surface structures can be complemented and enriched by coupling them to well-defined geometrical structures such as V-shaped grooves along which fluids can spread. With the presently available etching techniques already in use for semiconductor surfaces, highly precise and smooth channels can be produced.

From a thermodynamic point of view the fluid structures exposed to such inhomogeneous environments are characterized by a free energy which decomposes into a bulk contribution proportional to the volume, a surface contribution proportional to the exposed surface area, and a line contribution proportional to the linear extension of a chemical step or a groove. The local morphology of these films is determined by these line contributions whereas the bulk and surface contributions fix the boundary conditions in the normal and lateral directions, respectively. As a first step towards the ambitious goals formulated above some elementary building blocks for such lateral fluid structures have been studied theoretically in detail: the three-phase contact line of liquid, vapour and a solid [3], the morphology of a liquid film across a chemical step [4], wetting of a wedge [5], adsorption in grooves [6], and the effect of curvature on wetting films [7]. All these studies reveal a very rich thermodynamic behaviour with local structures which deviate strongly from the

corresponding homogeneous bulk phases. These findings promise that future theoretical analyses and thorough experimental tests will be very rewarding.

References

- [1] Dietrich S 1988 Wetting phenomena *Phase Transitions and Critical Phenomena* vol 12, ed C Domb and J L Lebowitz (London: Academic) p 1
- [2] Dietrich S and Haase A 1995 Scattering of x-rays and neutrons at interfaces *Phys. Rep.* **260** 1–138
- [3] Getta T and Dietrich S 1998 Line tension between fluid phases and a substrate *Phys. Rev. E* **57** 655–72
- [4] Koch W, Dietrich S and Napiórkowski M 1995 Morphology and line tension of liquid films adsorbed on chemically structured substrates *Phys. Rev. E* **51** 3300–17
- [5] Koch W, Napiórkowski M and Dietrich S 1992 Wedge wetting by van der Waals fluids *Phys. Rev. A* **45** 5760–70
- [6] Schoen M and Dietrich S 1997 Structure of a hard-sphere fluid in hard grooves *Phys. Rev. E* **56** 499–510
- [7] Bieker T and Dietrich S 1998 Wetting of curved surfaces *Physica A* **252** 85–137