

The hard physics of soft matter

H. Löwen, M. Watzlawek, C. N. Likos, M. Schmidt, A. Jusufi,
J. Dzubiella, C. von Ferber, E. Allahyarov, A. Thünemann, I. D'Amico⁺

Institut für Theoretische Physik II, Heinrich-Heine-Universität Düsseldorf,
Universitätsstraße 1, D-40225 Düsseldorf, Germany

⁺ present address: Department of Physics, University of Missouri, Columbia,
MO 65211, USA

Summary: By definition, soft matter systems react sensitively upon external mechanical perturbations. This material class includes mesoscopic complex fluids such as colloids, polymers and membranes. It is a major challenge to understand the fascinating properties of soft matter from first principles, i.e., by deriving its properties from the microscopic interactions. Here, concepts borrowed from statistical physics are described, which are capable to overbridge the gap from microscopic over mesoscopic to macroscopic length scales. This is illustrated explicitly for star polymer solutions and charged colloidal suspensions.

1 Introduction: What is meant by soft matter?

Soft matter [1] is synonymous with “complex fluids” and “colloids” although emphasis is put on different aspects in using these substitute names. The textbook definition of *colloids* is that there is at least one mesoscopic length scale in the range between 1nm and 1 μ m on which the system exhibit discontinuities. The main difference between a *molecular* and a *colloidal* system becomes immediately clear in comparing two liquids known from everyday life: corn schnapps and milk. Corn schnapps looks like a clear and structureless fluid on a length scale down towards nanometers and one needs molecular resolution to detect the water and alcohol molecules. Milk, on the other hand, consists of fat globules exhibiting already a structure on a length scale of 10 microns. Furthermore, milk contains submicron-sized caseine micelles which are the crucial building blocks in producing cheese. Hence the length scales of the characteristic structure are quite different in the two cases: schnapps is a molecular and milk a colloidal liquid.

Discontinuities on a mesoscopic scale can happen between different phases. Accordingly [2], there are eight different kinds of colloidal dispersions depending on whether the disperse phase and the dispersion medium are in the solid, liquid or gas phase. The name “colloids” is also frequently used in a more specialized sense for colloidal suspensions which are solid particles embedded in a molecular liquid. Typical examples are printing ink, paints, blood, urine, spittle, adhesives (e.g. glue where the name “colloid” stems from), viruses, and muddy water.

The physics of colloids is the domain between molecular physics occurring on a length scale smaller than one nanometer and the traditional solid state physics of small crystallites which are larger than a micron. As a characteristic feature of colloids, their bulk to interface ratio is much larger than that of a crystallite. This can readily be seen by cutting a macroscopic solid into subunits and counting the resulting area. Hence colloidal and interfacial properties are very much inter-related.

If the term *complex fluids* is used, emphasis is put on the complexity of the description which involves very different (microscopic and mesoscopic) length scales [3]. Finally, the expression *soft matter* puts emphasis on the mechanical properties of colloidal materials. They react sensitively on mechanical perturbations as compression or shear. An example is given below.

Let us first focus on colloidal suspensions, i.e., solid mesoscopic particles embedded in a molecular solvent. A theorist would immediately approximate the solid colloidal particles by isotropic spheres. This is of course the leading order in a systematic approximation of the particle shape but it is not that crazy as it looks at a first glance. By sophisticated preparation methods one is nowadays indeed able to realize excellent model suspensions of monodisperse submicron-sized latex or polystyrol spheres [4]. For high colloidal concentrations, these spheres self-organize in crystalline arrays, i.e., they undergo a freezing transition. Such a colloidal crystal has a lattice constant a in the mesoscopic regime which leads to different elastic properties as compared to molecular solids. This is illustrated strikingly by considering the shear modulus G of a colloidal crystal. Roughly speaking, G scales with a typical energy scale (say the thermal energy $k_B T$) divided by a typical volume of the elementary crystal cell, $G \approx k_B T/a^3$. Hence a colloidal crystal has a shear modulus which is 9-12 orders of magnitude smaller than that of an ordinary crystal! This implies that colloidal crystals are vulnerable to shear and explains why the term "soft matter" is appropriate for colloidal samples.

Polymers are other prominent examples of soft matter. They are macromolecules composed of many monomeric units. A typical example is a linear hydrocarbon chain. But there are more complicated topologies conceivable, such as branched polymers (called dendrimers) or star polymers which consist of f linear chains attached to a common microscopic center [5]. The monomers can be charged resulting in a highly charged macromolecule which is called polyelectrolyte.

One fascinating aspect of soft matter systems is that one can combine different building blocks to form new composite matter with novel material properties. This can be seen in analogy to the periodic table of the atoms by which molecules are formed. The important advantage for colloidal systems is, however, that the mixing procedure of the combination can be controlled much better by chemistry and the system itself helps by self-organization [6]. Following this route one may build self-assembled supramolecular matter on different hierarchies. In principle one can combine two self-organized combinations again reaching a higher hierarchy and so on. One exciting result of such a combination is a mixture of a positively charged polyelectrolyte and an ionic surfactant (characterized by a fluorinated head and an negatively charged tail) [7]. These mixtures self-organize in the presence of an external surface in multilamellar layers [8]. This induces an effective coating of the surface resulting in an ultra-low critical surface tension [9] even less than 11mN/m

[8, 10]. This novel coating opens the way for many interesting applications, such as protecting walls against graffiti sprayers, airplane wings against ice crystallization.

2 The theoretical challenge

2.1 General

From a more theoretical point of view, the great challenge in soft matter is to understand and predict the macroscopic properties starting from the microscopic interactions. Already for pure molecular systems such an “ab initio” calculation poses a very hard problem. For a soft matter system this is even more complicated due to the presence of intermediate mesoscopic length scales.

Typical target quantities are the osmotic pressure of a colloidal dispersion, the elastic moduli or the phase behavior of colloidal suspensions as a function of internal thermodynamic or external parameters. A general framework to overbridge the different length scales is highly desirable because: i) a fundamental understanding of the thermodynamics of soft matter including biological macromolecules can be reached and ii) new material properties could be predicted.

It is clear that methods of classical equilibrium statistical mechanics should be applicable as most of the constituents are described as classical particles. Bridging the different length scales is most conveniently done in different steps from microscopic to mesoscopic and then from mesoscopic to macroscopic length scales. The first step can be made by using the important concept of the effective interaction. The second step is performed using ideas from classical many-body theory. Let us first outline these concepts briefly in general and then illustrate them for star polymer solutions and charged colloidal suspensions, in particular.

2.2 The concept of the effective interaction

In order to illustrate the concept we assume that there are two species: microscopic and mesoscopic particles. The generalization to several microscopic and more macroscopic species is obvious. Assume that the classical Hamilton function H of the system involves N_1 big and N_2 small particles and can be written as

$$H = K_1 + K_2 + V_{11} + V_{12} + V_{22} \quad (2.1)$$

where the label 1 is for the big mesoscopic particles and the label 2 for the microscopic particles. Here

$$K_1 = \sum_{j=1}^{N_1} \frac{\vec{P}_j^2}{2M} \quad (2.2)$$

is the kinetic energy of the big and

$$K_2 = \sum_{j=1}^{N_2} \frac{\vec{p}_j^2}{2m} \quad (2.3)$$

the kinetic energy of the small particles, \vec{P}_j, \vec{p}_j denoting the momenta of the big and small particles. If the positions are denoted with \vec{R}_j and \vec{r}_j , respectively, the microscopic interactions between big-big, big-small and small-small are embodied in the potentials $V_{11} = V_{11}(\{\vec{R}_j\})$, $V_{12} = V_{12}(\{\vec{R}_j\}, \{\vec{r}_j\})$ and $V_{22} = V_{22}(\{\vec{r}_j\})$. Note that our argument holds for arbitrary interactions, not only for pairwise interactions.

The total canonical partition function Z is the Boltzmann average

$$Z = \langle\langle \exp(-\beta H) \rangle\rangle_2 \equiv \langle\langle \exp(-\beta H) \rangle\rangle_1 \rangle_2 \quad (2.4)$$

with the canonical averages of a quantity \mathcal{A} defined as

$$\langle \mathcal{A} \rangle_1 = \frac{1}{N_1!} \frac{1}{h^{3N_1}} \int_V d^3 R_1 \dots \int_V d^3 R_{N_1} \int d^3 P_1 \dots \int d^3 P_{N_1} \mathcal{A} \quad (2.5)$$

and

$$\langle \mathcal{A} \rangle_2 = \frac{1}{N_2!} \frac{1}{h^{3N_2}} \int_V d^3 r_1 \dots \int_V d^3 r_{N_2} \int d^3 p_1 \dots \int d^3 p_{N_2} \mathcal{A} \quad (2.6)$$

Here V is the system volume, h is Planck's constant and $\beta = 1/k_B T$ is the inverse thermal energy.

We now define an *effective Hamiltonian* H_{eff} which only involves the coordinates of the big particles by requiring

$$Z = \langle \exp(-\beta H_{\text{eff}}) \rangle_1 \quad (2.7)$$

As can directly be verified by insertion, H_{eff} has the following form

$$H_{\text{eff}} = K_1 + V_{11} - \frac{1}{\beta} \ln[\langle \exp(-\beta(K_2 + V_{12} + V_{22})) \rangle_2]. \quad (2.8)$$

such that

$$V_{\text{eff}} = V_{11} - \frac{1}{\beta} \ln[\langle \exp(-\beta(K_2 + V_{12} + V_{22})) \rangle_2], \quad (2.9)$$

is the total effective potential energy of the big particles. The first term is the direct interaction while the second term is the logarithm of the micro-particle averaged Boltzmann factor, the so-called potential of mean-force. In fact, the effective forces acting on the big particle are obtained by taking the gradient of V_{eff} with respect to the particle coordinate. As a further comment, the statistical average

$$\bar{\mathcal{A}} = \langle\langle \mathcal{A}(\vec{R}_1, \dots, \vec{R}_{N_1}) \exp(-\beta H) \rangle\rangle_2 \quad (2.10)$$

of any quantity depending only on the positions of the big particles $\vec{R}_1, \dots, \vec{R}_{N_1}$ can be calculated by using H_{eff} alone, i.e.

$$\bar{\mathcal{A}} = \langle \mathcal{A}(\vec{R}_1, \dots, \vec{R}_{N_1}) \exp(-\beta H_{\text{eff}}) \rangle_1. \quad (2.11)$$

Calculating V_{eff} requires a micro-particle average. Once this has been performed, the small particles are traced out and all the microscopic degrees have dropped out of sight. Hence this concept provides a bridge between microscopic and mesoscopic length scales.

2.3 Many-body theory

In general, the effective potential involves many-body forces even if the starting interactions are pairwise. In many (but not all) practical situations, however, it turns out that the triplet and higher-order contributions to the effective interactions are small and negligible. Then, on the level of the mesoscopic length scales, the problem is a classical many-body system with a pairwise interaction held at fixed temperature and at given concentration.

There are many powerful statistical methods, including liquid state theory [11], solid cell models, density functional theory [12] or direct computer simulation methods [13] to proceed further. In doing so, there is a complete formal analogy to classical atomic systems as e.g. argon gas, only the inherent length scale is mesoscopic in our problem.

3 Star polymer solutions

A solution of star polymers at finite concentration involves indeed many different length scales ranging from the microscopic to the macroscopic regime. They are sketched in Fig. 1: On the full microscopic level, there are solvent molecules and hydrocarbon chains (Fig. 1a). Zooming out, the next relevant length scale is the persistence length of a single linear chain shown in Fig. 1b. The next larger relevant length scale is the spatial extension of a single star, the so-called corona diameter σ as shown in Fig. 1c. Then the average separation between two stars at finite star number density ρ governs the inter-star correlations (Fig. 1d). Last, the size of the sample is determined by a macroscopic scale (Fig. 1e).

Bridging from (1a) to (1b) is done using polymer scaling theory [14]. This implies that microscopic details are not relevant on larger scales since the chains are very long. Using this together with the concept of the effective potential, one can integrate out the microscopic monomers. Applying the formalism of section IIb, the monomers are the small particles and the star *centers* represent the big particles. Thus, bridging the gap from (1b) to (1d), one obtains the following effective interparticle pair potential between the star centers:

$$V(r) = \begin{cases} \frac{5}{18} k_B T f^{3/2} \left[-\ln\left(\frac{r}{\sigma}\right) + \frac{1}{1+\sqrt{f/2}} \right] & \text{for } r \leq \sigma \\ \frac{5}{18} k_B T f^{3/2} \frac{\sigma}{1+\sqrt{f/2}} \frac{\exp(-\sqrt{f}(r-\sigma)/2\sigma)}{r} & \text{for } r > \sigma \end{cases} \quad (3.12)$$

where r is the intercore distance between two stars such that

$$V_{\text{eff}} = \sum_{i,j(i<j)}^{N_1} V(|\vec{R}_i - \vec{R}_j|) \quad (3.13)$$

Here, f is the arm number of a single star. Evidence for this effective potential comes from the following observations: (i) The behavior for very small r ($r \ll \sigma$) is consistent with scaling theory [15, 16]. (ii) Microscopic Molecular Dynamics computer simulations have been performed for several values of f and different

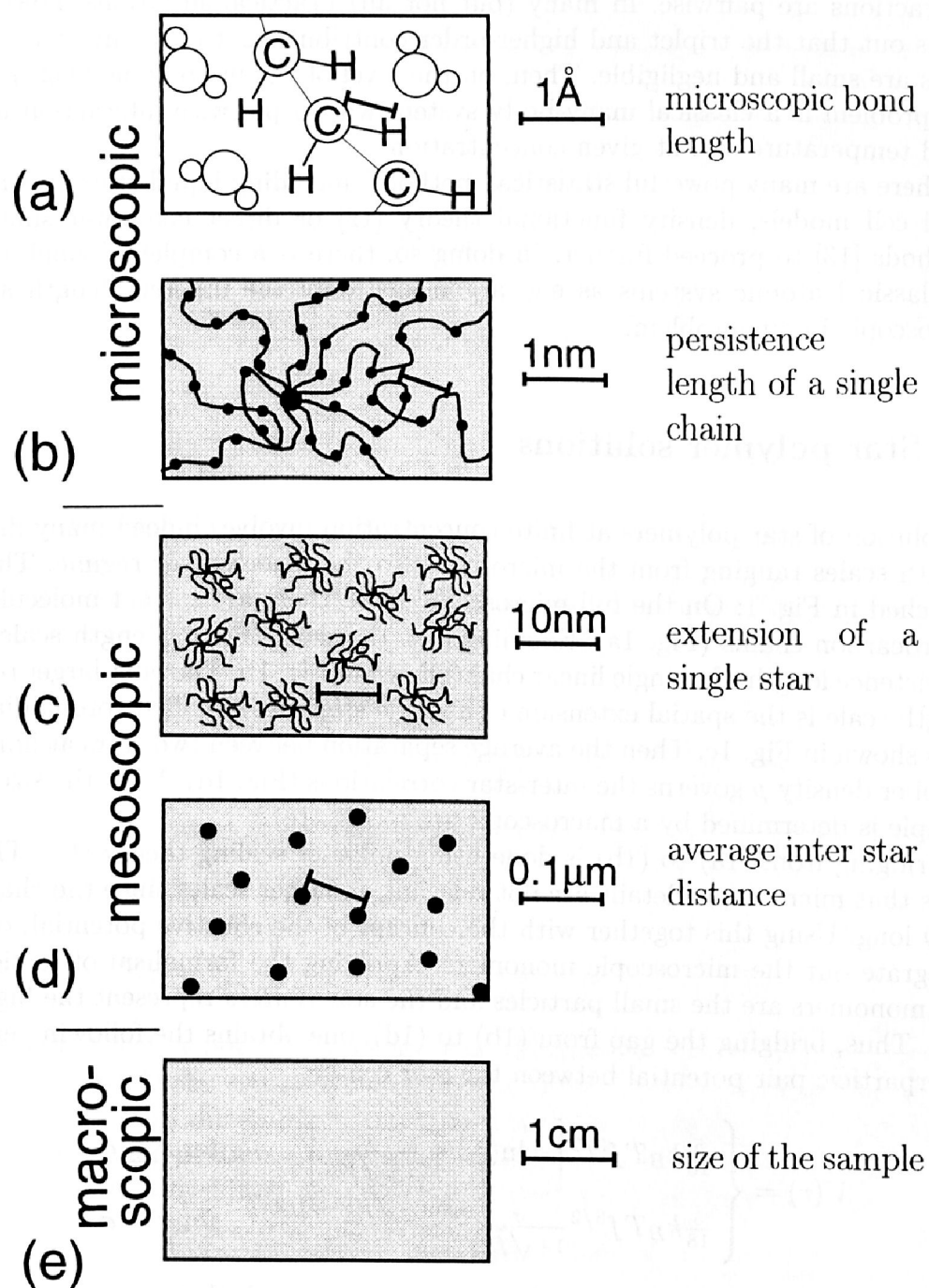


Figure 1 Star polymer solution on different length scales. (a): microscopic picture, water and hydrocarbon chains are shown, the chemical bonds have a range of typically 1\AA . (b): On a larger scale, the persistence length of a single chain is relevant. (c): the spatial extension σ of a single star. (d): all the stars are point particles on this scale governed by the mean intercore distance (e): size of the macroscopic sample.

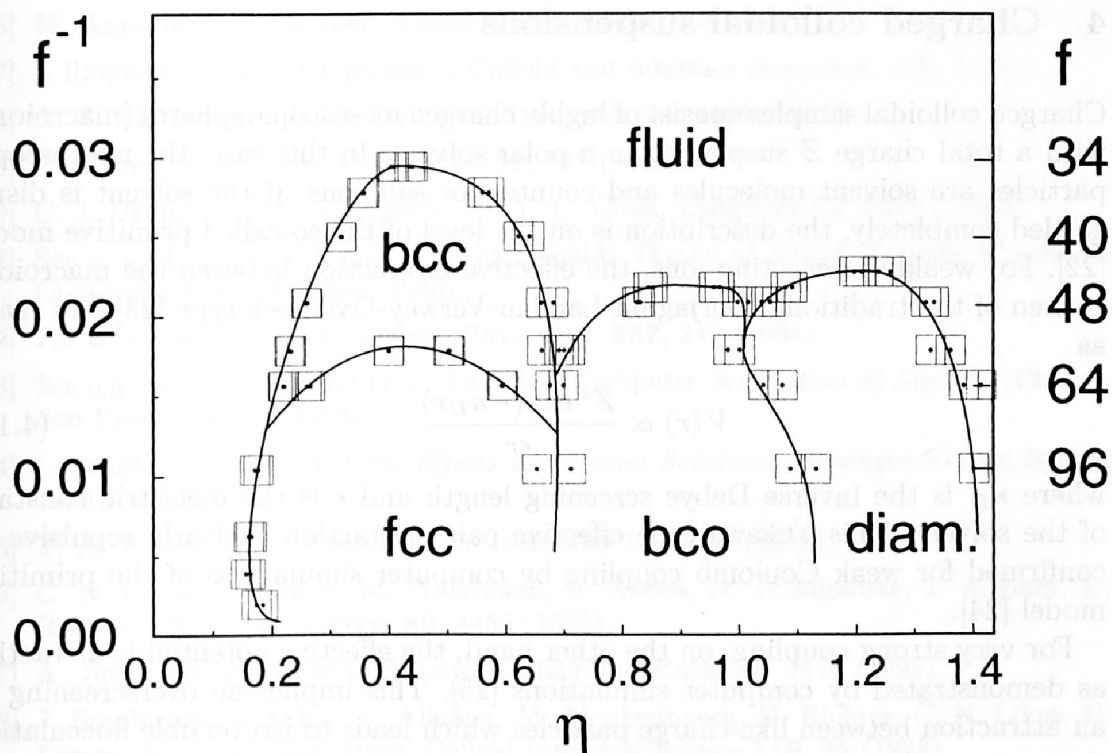


Figure 2 The phase diagram of star polymer solutions for different arm numbers f versus reduced density η . The squares are the results from computer simulation and mark coexistence conditions. The lines are a guide to the eye.

monomer numbers per chain [17]. They reproduce perfectly the overall shape of the effective interaction. (iii) For an 18-arm star, the intensity of small-angle neutron scattering data could be well-described by this pair potential [16, 18]. (iv) Triplet and higher-order correction were shown to be small even if the concentration is above overlap $\rho > 1/\sigma^3$ [19]. The next step is from (1d) to (1e) which can be done with a computer simulation involving 100-10000 stars treated as structureless classical particles. The phase diagram of a star polymer solution in a good solvent was obtained in the plane spanned by the reduced density $\eta = \pi\rho\sigma^3/6$ and the inverse arm number $1/f$ [20]. Results are displayed in Fig. 2. Remarkably, there is no freezing below a critical arm number $f_c \approx 34$. For $f > f_c$ there is freezing, with increasing density, into a body-centered-cubic (bcc) lattice, which then remelts upon further compression. For higher arm numbers, freezing into a face-centered-cubic (fcc) lattice occurs, since the potential is becoming steeper as f is increasing. For higher densities, however, there are less common solid structures: an anisotropic body-centered orthorhombic phase as well as a diamond lattice become stable. A very peculiar behavior occurs for intermediate arm number $f \approx 48$: Increasing the density, the system first freezes, then remelts, then refreezes again. Such behavior also has been found experimentally in spherical diblock copolymer micelles by Gast and coworkers [21].

4 Charged colloidal suspensions

Charged colloidal samples consist of highly charged mesoscopic spheres (macroions) with a total charge Z suspended in a polar solvent. In this case, the microscopic particles are solvent molecules and counter- or salt ions. If the solvent is disregarded completely, the description is on the level of the so-called primitive model [22]. For weakly interacting ions, the effective interaction between the macroions is then of the traditional Derjaguin-Landau-Verwey-Overbeek type [23] and reads as

$$V(r) \propto \frac{Z^2 \exp(-\kappa_D r)}{\epsilon r}, \quad (4.14)$$

where κ_D is the inverse Debye screening length and ϵ is the dielectric constant of the solvent. This Yukawa-type effective pair interaction is clearly repulsive as confirmed for weak Coulomb coupling by computer simulations of the primitive model [24].

For very strong coupling, on the other hand, the effective potential is attractive as demonstrated by computer simulations [25]. This implies an overscreening or an attraction between like-charge particles which leads to irreversible flocculation destroying colloidal stability in a macroscopic sample. So here again the concept of the effective potential is a powerful tool in predicting macroscopic behavior.

5 Conclusions

The physics and the theoretical description of soft matter is hard since many different length (and time) scales are involved. We have shown that tricks from classical statistical mechanics can be used to overbridge the different scales in order to get a full microscopic understanding. This was illustrated for star polymer solutions and charged colloidal suspensions. As a result, new unusual phase behavior was obtained which could be traced back to the peculiar feature of the effective interaction generated by the collective average of the microscopic species.

Bibliography

- [1] For a recent review, see: T. A. Witten, *Rev. Mod. Phys.* **71**, 367 (1999).
- [2] R. J. Hunter, *Foundations of Colloid Science*, Volume I, Oxford Science Publications, Clarendon Press, Oxford, 1989.
- [3] De Gennes who gained the nobel prize in soft matter theory in 1991, however, stressed in his nobel speech that "complex fluids is an ugly name which tends to discourage the young students".
- [4] See e.g.: S. Nesper, C. Bechinger, P. Leiderer, T. Palberg, *Phys. Rev. Letters* **79**, 2348 (1997).
- [5] For a review see: G. S. Grest, L. J. Fetters, J. S. Huang, D. Richter, *Advances in Chemical Physics*, Volume XCIV, 67 (1996).

- [6] M. Antonietti, C. Göltner, *Angew. Chemie* **109**, 944 (1997).
- [7] I. Iliopoulos, *Current Opinion in Colloid and Interface Science* **3**, 493 (1998).
- [8] A. F. Thünemann, K. H. Lochhaas, *Langmuir* **14**, 4898 (1998).
- [9] P. G. de Gennes, *Rev. Mod. Phys.* **57**, 827 (1985).
- [10] C. J. Drummond, G. Georgaklis, D. Y. C. Chan, *Langmuir* **12**, 2617 (1996).
- [11] See e. g. J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids*. 2^d edition (Academic Press, London, 1986).
- [12] For a review see e.g.: H. Löwen, *Phys. Rep.* **237**, 249 (1994).
- [13] See e.g.: M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids*. (Clarendon Press, Oxford, 1989).
- [14] L. Schäfer, *Excluded Volume Effects in Polymer Solutions*. (Springer-Verlag, Berlin, 1999).
- [15] T. A. Witten, P. A. Pincus, *Macromolecules* **19**, 2509 (1986).
- [16] C. N. Likos, H. Löwen, M. Watzlawek, B. Abbas, O. Jucknischke, J. Allgaier, D. Richter, *Phys. Rev. Letters* **80**, 4450 (1998).
- [17] A. Jusufi, M. Watzlawek, H. Löwen, *Macromolecules* **32**, 4470 (1999).
- [18] J. Stellbrink, B. Abbas, J. Allgaier, M. Monkenbusch, D. Richter, C. N. Likos, H. Löwen, M. Watzlawek, *Prog. Colloid Interface Science* **110**, 25 (1998).
- [19] C. von Ferber, A. Jusufi, M. Watzlawek, C. N. Likos, H. Löwen, to be published in *European Physical Journal E* (2000).
- [20] M. Watzlawek, C. N. Likos, H. Löwen, *Phys. Rev. Letters*. **82**, 5289 (1999).
- [21] G. A. McConnell, A. P. Gast, *Macromolecules* **30**, 435 (1997).
- [22] J. P., Hansen, H. Löwen, *Annual Reviews of Physical Chemistry*, in press, October 2000.
- [23] B. V. Derjaguin, L. D. Landau, *Acta Physicochim. USSR* **14**, 633 (1941); E. J. W. Verwey and J. T. G. Overbeek, *Theory of the Stability of Lyophobic Colloids*. (Elsevier, Amsterdam, 1948).
- [24] I. D'Amico, H. Löwen, *Physica A* **237**, 25 (1997).
- [25] E. Allahyarov, I. D'Amico, H. Löwen, *Phys. Rev. Letters* **81**, 1334 (1998).