SCATTERING FROM SHEAR-ORDERED DISPERSIONS

H. VERSMOLD

Institut für Physikalische Chemie, RWTH Aachen, 52056 Aachen, Germany

E-mail: versmold@pc.rwth-aachen.de
Fax: x49.241.8092327

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ABSTRACT:
Rheology is commonly used as a tool for analytics and quality control in latex technology. As soon as flow becomes essential for the structure measured in a scattering experiment we call it scattering from shear-ordered dispersions or rheologic scattering. In this paper it is shown that the structure of concentrated dispersions can with advantage be studied by scattering experiments. Theoretical and experimental aspects as well as examples of small-angle synchrotron x-ray and neutron scattering from colloidal dispersions, presented in the paper, are closely related to rheology.

ZUSAMMENFASSUNG:
Rheologie wird in der Latextechnologie für analytische Zwecke und zur Qualitätskontrolle eingesetzt. Sobald durch Fliessen in einem Streuexperiment die Struktur einer Dispersion beeinflusst wird, sprechen wir von „Streuung durch schergeordnete Dispersionen“ oder „Rheologischer Streuung“. In dieser Arbeit wird gezeigt, dass die Struktur von Dispersionen vorteilhaft durch Streuexperimente untersucht werden kann. Es werden theoretische und experimentelle Aspekte der Synchrotronröntgen- und Neutronenstreuung von konzentrierten Dispersionen behandelt, die eng mit der Rheologie verwandt sind.

RÉSUMÉ:
La rhéologie est communément employée comme outil de contrôle de qualité et d’analyses dans la technologie des latex. Aussitôt que l’écoulement devient essentiel pour la structure mesurée lors d’une expérience de diffusion, nous l’appelons diffusion à partir de dispersions ordonnées par cisaillement ou diffusion rhéologique. Dans cet article, il est démontré que la structure de dispersions concentrées peut être avantageusement étudiée à l’aide d’expériences de diffusion. Des aspects théoriques et expérimentaux, ainsi que des exemples de diffusion de neutrons et de rayons X synchrotron aux petits angles par des dispersions colloïdales présentés dans cet article, sont intimement reliés à la rhéologie.

KEY WORDS: Charge-stabilized latex dispersions, scattering, structure, rheology

1 INTRODUCTION

Although scattering from shear-ordered dispersions is different from rheology [1,2] these two techniques resemble each other. Beside many other applications rheology is also used as a tool for analytics and quality control in latex technology. In this paper the influence of flow on the scattering from latex dispersions will be considered. Usually scattering experiments are carried out with the sample at rest. As soon as flow becomes essential for the structure in a scattering experiment, we call it scattering from shear-ordered dispersions or rheologic scattering. It will be shown that the influence of flow on the structure of concentrated dispersions can be used in several ways:

1. Ordering the sample by flow, but keeping it at rest for the measurement. After a sufficiently long waiting time, the sample will often be crystalline. This technique allows to measure the stacking order at rest and the kinetics of crystal growth.
2. one can again start with a layered sample. This also allows to measure the structure and the stacking of layers through the viscoelastic transition under flow.

Because rheology is commonly carried out under flow only the second structure, the layers, can be analyzed by rheology. Rheology seems to be sufficient for many applications. However, as one gets interested in structural details scattering experiments become obligatory. We under-

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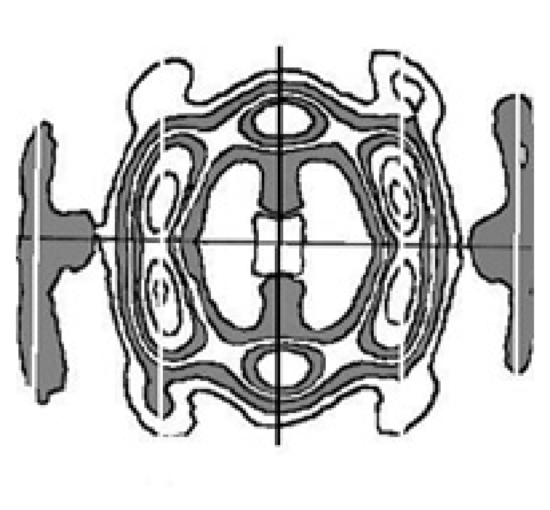

Figure 10 (left above): Neutron scattering from a latex film (Redrawn after [20]).

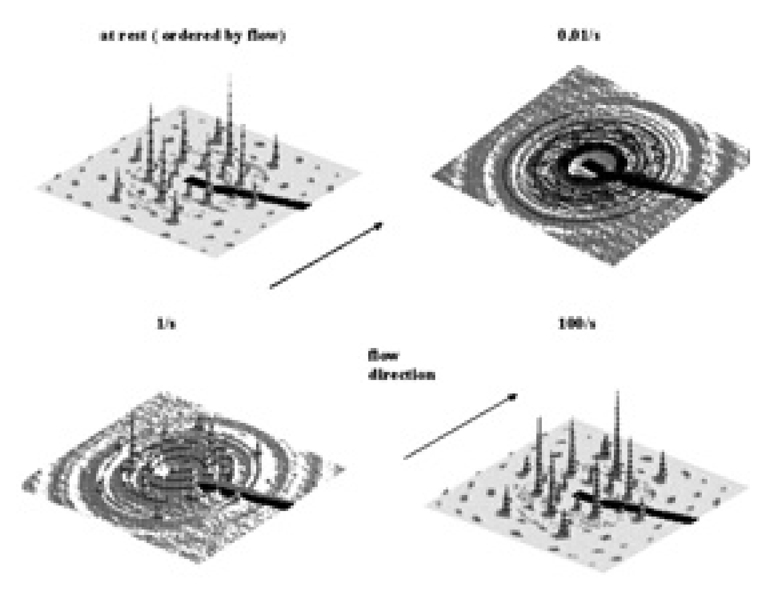

Figure 9 (right above): Synchrotron x-ray scattering (SAXS) of the viscoelastic transition.

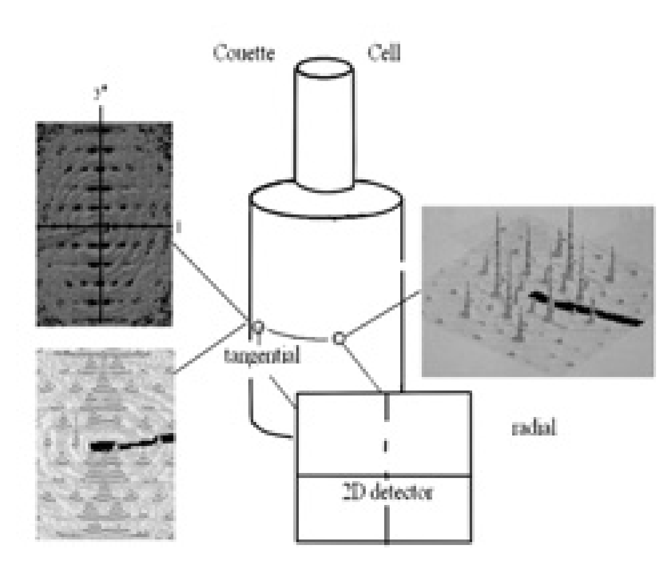

Figure 11 (below): Synchrotron x-ray scattering (SAXS) on the anisotropy of a concentrated dispersion.

layers of particles are assumed to exist. The stacking in the film should be measurable by tangential scattering as described above. In Figure 10 the step-by-step neutron scattering result of film formation with latex particles of Joanicot, Lindner, and Cabane [20] is redrawn. Although the scattering is not perfectly tangential (tilted by 11°), the black-white-white-black structure of the Bragg rods is clearly indicated. Further a splitting similar to the fcc intensity can be seen on the rods next to the central black l = 0,0 rod. The experiment deserves to be repeated and should also be carried out by synchrotron x-ray scattering.

Next, we consider Figure 11 which shows the radial and tangential x-ray scattering from a Couette cell filled with a concentrated (30 vol%) charge-stabilized latex dispersion of particle diameter σ ~ 100 nm. Although both types of scattering (radial and tangential) were collected Figure 11 under similar conditions, it is important to note that the radial scattering (picture on the right hand side) and the tangential scattering (pictures on the left hand side) are vastly different. From this behavior we must conclude that such a concentrated dispersion is not isotropic. This is also different from ordinary liquids for which the result of a scattering experiment should not depend on the orientation of the sample.

Because highly dilute dispersions have been found to be liquid-like and isotropic [3] the property of being anisotropic seems to be related to the concentration of the dispersion. The behavior resembles the one of liquid crystals [21] . For example liquid crystals show an anisotropy already at rest. They order spontaneously. By contrast, for cubic colloidal crystals shear ordering appears to be necessary for the anisotropy to be visible. At present it is unknown at which concentration such a system becomes anisotropic. Also the magnitude of the necessary shear is unknown.

4 DISCUSSION AND SUMMARY

Many of the structural properties of a charge-stabilized dispersion are commonly investigated by rheology. As the present paper shows structural properties should also be studied by scattering experiments. The fact that concentrated dispersions are not transparent can be overcome by scattering experiments with more penetrable radiation than light. Of particular value for concentrated dispersions are small-angle neutron and small-angle synchrotron x-ray scattering experiments.

At perpendicular incidence (radial for the Couette cell) under flow the structure in the flow

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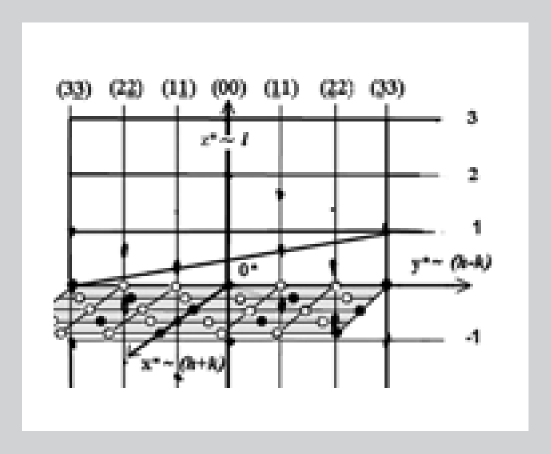

Figure 12: Results of the radial (dark plane) and tangential (in the background) synchrotron x-ray scattering from a Couette cell, obtained for an about 30 vol% concentrated fcc single crystal (F ~ 100 nm).

generated *h*, *k* layers can be measured. At this perpendicular beam incidence also the viscoelastic properties of a dispersion can be investigated. The viscoelasticity is visible in a limited range of shear rates and can be identified by rings in the scattering intensity [13]. In this paper we have shown that measurement of the Miller index *l*-dependence of the scattering intensity along several *h*, *k* rods provides very interesting information on the stacking of layers which to a certain degree is complementary to the information obtained from rheology.

There are two methods to study the stacking of layers by scattering: An old one which consists of sample rotation defines the rotation or step-by-step method. A more recent small-angle method, tangential scattering [12], works without sample rotation.

A summary of our findings by synchrotron x-ray scattering from a fcc single crystal is given in Figure 12. The *x**, *y** layer is drawn darker and perpendicular to the black (3,-3; 0,0; -3,3) and grey (2,-2; 1,-1; -1,1; -2,2) Bragg rods. The experimental tangential synchrotron x-ray scattering intensity of a fcc single crystal is shown in the background. The intensity in the *l*-direction (the direction of the rods) shows a clean *l* = 1/3, *l* = 2/3 (= -1/3) dependence on the twin rods 1,-1 = 1, $\underline{1}$ and -1,1 = $\underline{1}$,1. In general the intensity along the rods depends on the stacking structure of the layers and on the kinetics of the layer exchange which are not investigated in detail at present.

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