

# STRUCTURAL STUDIES OF MIXED NANO-SPHERES AND POLYMERS

ESTUDIOS ESTRUCTURALES EN MEZCLAS DE NANO-ESFERAS Y POLÍMEROS

A. WASHINGTON<sup>a</sup>, X. LI<sup>a</sup>, A. SCHOFIELD<sup>c</sup>, K. HONG<sup>b</sup>, M. R. FITZSIMMONS<sup>e</sup> AND R. PYNNE<sup>a,b,d</sup>

a) Center for the Exploration of Energy and Matter, and Indiana University Department of Physics, Bloomington, Indiana, USA

b) Center for Nanophase Materials Science, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA

c) School of Physics and Astronomy, University of Edinburgh, Mayfield Road, Edinburgh, Scotland

d) Center for Advanced Studies, Norwegian Academy of Science and Letters, Oslo, Norway

e) Los Alamos National Laboratory, Los Alamos, New Mexico, USA

A newly developed neutron scattering technique known as Spin Echo Small Angle Neutron Scattering (SESANS) allows real-space density correlations to be probed in bulk samples over distances ranging from  $\sim 20$  nm to up to several microns. We have applied this technique to study correlations between polymer-stabilized poly(methyl methacrylate) (PMMA) spheres suspended in either dodecane or decalin. As expected, the data show that for colloid volume fractions below about 40%, correlations between PMMA spheres are accurately described by the Percus-Yevick hard-sphere model. When a small amount of polymer is added to the colloidal suspension and when the carrier fluid is a good solvent for the polymer, short-range correlations between PMMA spheres are increased by the presence of the polymer depletant and are in reasonably agreement with calculations using an integral equation model. When higher concentrations of polymers are added, we find that long-range, power-law correlations develop between spheres, even though the sample flows freely. When the solvent is not a good solvent for the polymer depletant, correlations between PMMA spheres are unaffected by the addition of small quantities of polymer.

Una nueva técnica de dispersión de neutrones conocida como espín-eco de dispersión de neutrones de bajo ángulo (SESANS, según sus siglas en inglés) permite medir correlaciones de densidad en el espacio real, para muestras masivas, sobre distancias que van desde unos 20 nm, hasta algunas micras. Hemos aplicado esta técnica al estudio de las correlaciones entre esferas poliméricas estabilizadas de polimetil-metacrilato (PMMA) suspendidas en dodecano o decalina. Como se espera, los datos muestran que, para fracciones volumétricas inferiores al  $\sim 40\%$ , las correlaciones entre las esferas de PMMA se describen bien por el modelo de Percus-Yevick de esferas-rígidas. Cuando se adiciona una pequeña cantidad de polímero a la suspensión coloidal, y cuando el fluido portador es un buen solvente para el polímero, se incrementan por la presencia del depletante de polímero, y muestran un acuerdo razonable con cálculos según un modelo basado en una ecuación integral. Cuando se usan concentraciones mayores de polímero, encontramos correlaciones de largo alcance entre esferas, del tipo ley de potencia, aún cuando la muestra fluye libremente. Cuando el solvente no disuelve bien el depletante de polímero, las correlaciones entre esferas no se afectan si se agregan pequeñas cantidades de polímero.

**PACS:** Neutron scattering in structure determination, 61.05.fg; polymer solutions flow properties, 47.57.Ng; structure of polymer solutions, 61.25.he; correlations collective effects, 71.45.Gm

## INTRODUCTION

When sterically-stabilized colloidal spheres of poly(methyl methacrylate) (PMMA) are suspended in a hydrocarbon solvent, small angle neutron scattering (SANS) from the mixture can be described using the Percus-Yevick model for hard-sphere correlations [1]. In the present work, our goal was to probe the changes induced in the correlations between the colloidal spheres when an attractive force between them is turned on. To generate this force, we have added small amounts of polymer to generate a depletion interaction between the spheres [7]. Rather than measure the correlations using traditional SANS, we have chosen to use a new technique called spin-echo SANS or SESANS.

## SESANS AND SANS

SANS is a widely used method for interrogating the structure

of materials on length scales between a few nanometers and roughly 100 nm. SANS measurements of a colloidal fluid are described as a product of a form factor –the Fourier transform of the density distribution within each colloidal particle– multiplied by a structure factor which contains information about inter-particle correlations. Unfortunately, much of the latter information is found at large values of the neutron's wavevector transfer,  $Q$ , where the scattering is strongly damped by the form factor. This makes traditional SANS a good tool for measuring form factors, i.e. the structure of non-interacting monodisperse particles, but a rather poor one for measuring inter-particle correlations in colloids.

SESANS overcomes some of the disadvantages of SANS by Fourier transforming the neutron scattering signal and providing a correlation function in real space [2]. It is

more sensitive to inter-particle correlations than traditional SANS because it exactly Fourier transforms the scattering signal –including the weak signal at large  $Q$  which contains information about correlations– before noise is added by the measurement. In addition to this advantage, SESANS measures the same pair correlation function even when a sample scatters strongly whereas SANS patterns obtained with concentrated, strongly scattering dispersions have to be corrected for multiple scattering of neutrons. Finally, the length scale probed by SESANS is larger than for SANS, which makes it a good tool for exploring correlation functions in colloidal fluids containing particles of a few hundred nanometers in diameter.

The correlation function,  $G(z)$ , measured by SESANS is a projection of the usual Debye density-autocorrelation function on to a particular direction,  $z$ . For isotropic fluids such as those studied here the choice of direction onto which the Debye function is projected is irrelevant. Mathematically,  $G(z)$  is given by the Abel transform of the Debye correlation function [5].

SESANS works by encoding the scattering angle of each neutron into the Larmor precession phase accumulated as the neutron passes through suitably designed magnetic fields [6]. In a SESANS experiment, the cosine of the total Larmor phase is averaged over the scattered neutron beam and measured as a neutron polarization. Because of the cosine factor, the neutron polarization represents a Fourier transform of the scattered neutron intensity.

We have constructed a SESANS apparatus that can be installed on neutron scattering instruments that provide a polarized neutron beam and the measurements described here have been obtained with this equipment mounted on the Asterix reflectometer at the Los Alamos Neutron Science Center (LANSCE). An account of the SESANS technique, which includes a description of the apparatus used in the measurements described here, is given in reference [6].

## RESULTS

The colloidal samples we have used in our experiments were prepared using a published method [3]. The resulting PMMA particles, which had diameters between 200 nm and 250 nm depending on the sample batch, were suspended in either dodecane or decalin at concentrations between 30% and 50% by volume. In order to adjust the neutron scattering contrast between the PMMA spheres and the carrier fluid, mixtures of deuterated and hydrogenated solvents were used. Decalin is both a reasonable solvent for the polymer depletant used in our experiments (polystyrene) and has an optical refractive index which is close to that of PMMA, ensuring that the van der Waals interactions between the PMMA spheres is minimized. Dodecane, on the other hand, is a relatively poor solvent for polystyrene. For PMMA concentrations up to at least 40% by volume, SESANS shows that the correlations between PMMA

particles in freshly sonicated samples are well described by the Percus-Yevick, hard-sphere theory for both dodecane and decalin solvents, as shown in Figures 1 (a) and 1 (b).

When small concentrations of polymer depletant are added, the short-range correlations between particles are increased when they are suspended in decalin. A calculation using integral-equation theory [4] shows that the data in Figure 1 (a) can be described using a short-range, attractive potential that is roughly  $2kT$  deep. The magnitude of this potential appears to be approximately the same for polymer molecular weights of 110 kDa and 900 kDa when the same weight percentage of polymer depletant is used. When the particles are dispersed in dodecane, the addition of polystyrene does not change the inter-particle correlations, at least for polystyrene concentrations up to 1% by weight (cf. Figure 1 (b)). This is probably due to the fact that the PS molecules tend to collapse in the poor solvent, significantly reducing the depletion forces.

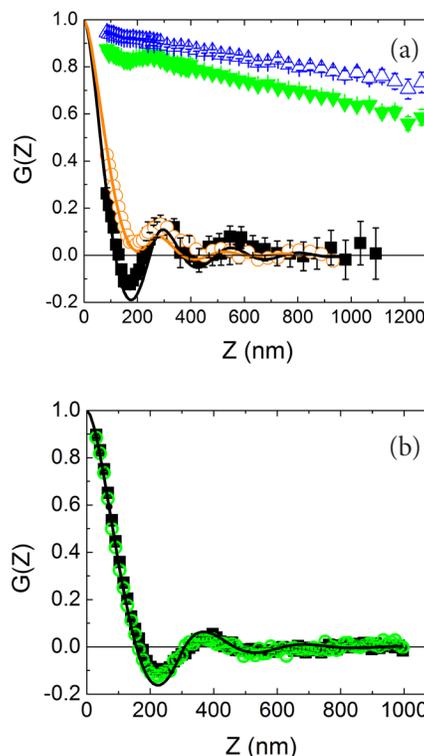


Figure 1: (a) The inter-particle correlation function  $G(z)$  for 40% suspensions of 260-nm-diameter PMMA spheres in decalin measured by SESANS. Solid squares –PMMA spheres alone; open circles– PMMA with 0.2% 900 kDa polystyrene; open triangles PMMA with 1% 900 kDa polystyrene; inverted triangles PMMA with 0.5% 900 kDa polystyrene. Dark line is Percus-Yevick calculation and the lighter line is result of integral equation calculation with “sticky” spheres. (b)  $G(z)$  for a 40% suspension of PMMA spheres in dodecane (solid squares) and with 1% 110 kDa polystyrene (open circles). The line is calculated from the Percus-Yevick theory.

For larger concentrations of depletant in the decalin system (greater than roughly 0.3% by weight for polymers with molecular weights of either 110 kDa or 900 kDa), SESANS indicates that correlations extend out to distances of many particle diameters and that the correlation function  $G(z)$  is roughly a linear function over much of the range of inter-particle distances probed (cf. Figure 1 (a)). The correlations

eventually disappear at sufficiently large values of  $z$ , indicating the maximum size of the aggregates that have been formed. The linear behavior of  $G(z)$  is consistent with a power-law behavior of the Debye correlation function. Although the maximum aggregate size often increases with time over periods of several hours, aggregates can be broken up easily by stirring and sonication. The short-range correlations in aggregates appear to be independent of aggregate size but are slightly different from those obtained with weak sticky potentials that do not result in aggregates. This presumably results from jamming of particles once aggregates are formed.

#### ACKNOWLEDGEMENTS

This work was funded by the U.S. Department of Energy through its Office of Basic Energy Sciences, Division of Material Science and Engineering (Grant No. DE-FG02-09ER46279). The Los Alamos Neutron Science Center is funded by the U.S. Department of Energy's Office of Basic Energy Sciences under contract DE-AC52-06NA25396 with Los Alamos National Security LLC. Some of the sample preparation was done at the Center for Nanophase Materials Science at Oak Ridge National Laboratory, which is sponsored by the Office of Basic Energy Sciences, U.S. Department of Energy.

- 
- [1] A. Moussaid, W. C. K. Poon, P. N. Pusey and M. F. Soliva, *Phys. Rev. Lett.* **82**, 225 (1999).
  - [2] R. Pynn, M. R. Fitzsimmons, H. Fritzsche, M. Gierlings, J. Major and A. Jason, *Rev. Sci. Instrum.* **76**, 053902 (2005).
  - [3] L. Antl, J. W. Goodwin, R. D. Hill, R. H. Ottewill, S. M. Owens, S. Papworth, and J. A. Waters, *Colloids And Surfaces* **17**, 67 (1986).
  - [4] X. Li, C. -Y. Shew, Y. Liu, R. Pynn, E. Liu, K. W. Herwig, G. S. Smith, J. L. Robertson and W. -R. Chen *J. Chem. Phys.* **132**, 174509 (2010).
  - [5] R. Andersson, L. F. Van Heijkamp, I. M. De Schepper and W. G. Bouwman., *J. Appl. Cryst.* **41**, 868 (2008).
  - [6] R. Pynn, R. Ashkar, P. Stonaha, A. L. Washington, *Physica B* **406**, 2350 (2011).
  - [7] W. C. K. Poon, *J. Phys: Condensed Matter* **14**, R859 (2002).