Properties of CdSe nanocrystal dispersions in the dilute regime: Structure and interparticle interactions

Hedi Mattoussi^{*} and Andrew W. Cumming Department of Physics, University of Florida, 215 Williamson Hall, Gainesville, Florida 32611

Christopher B. Murray[†] and Moungi G. Bawendi

Department of Chemistry, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, Massachusetts 02139

Raymond Ober

Laboratoire de Physique de la Matière Condensée, Collège de France, 11 place Marcellin Berthelot, 75231 Paris Cedex 05, France (Received 17 April 1997)

We report an investigation of the properties of CdSe nanocrystal dispersions using small-angle x-ray scattering. These nanocrystals are prepared from organometallic precursors using high-temperature solution chemistry. The study provides direct and accurate measures of the nanocrystal size and size distribution. The low polydispersity measured confirms the high quality of the nanocrystals prepared using a high-temperature solution chemistry route, as anticipated from optical data. The study also provides information on the interparticle interactions and their dependence on a few relevant parameters, such as nature of the capping molecules and solvent. Nanocrystal association, e.g., dimers, in dispersions characterized by weakly attractive interactions, and/or aggregation in solutions with strong attractions, can be observed. The study also unveiled other features where interactions are reversed from repulsive stabilizing to attractive as the particle size is decreased. This behavior, unexpected for colloidal dispersions, may be caused by a reduction of the cap density as the size is decreased. The general trend for the interparticle interactions in these dispersions can be understood within the framework of a van der Waals core to core attractive potential, to which are superposed effects of cap affinity to the core and to the surrounding solvent. Within these considerations, one can distinguish three types of dispersions: sterically stabilized dispersions, dispersions thermodynamically stable but governed by weak attractions, and unstable dispersions where strong attractions induce macroscopic aggregation. [S0163-1829(98)04335-5]

I. INTRODUCTION

Semiconductor nanocrystals (quantum dots or quantum crystallites) are small colloids with sizes that vary between 10 and 60 Å in radius.¹⁻⁴ Three-dimensional spatial confinement of electronic and vibrational excitations dominate the physical properties of these materials because their size is comparable to, or smaller than, the bulk Bohr exciton radius.^{5–8} For example, the widely reported blueshift of the energy band gap with decreasing size results from those confinement effects.¹⁻⁸ Spectroscopic properties, e.g., photoluminescence, also depend on the crystallite size, in addition to other parameters such as core crystallinity and particle shape.⁹⁻¹⁸ In the past decade, considerable effort has been devoted to understanding the effects of quantum confinement on the spectroscopic properties of these materials, using techniques such as photoluminescence, fluorescence line narrowing (FLN), cathodoluminescence, electroluminescence, and energy transfer.^{1–18}

These materials are prepared in solutions, for example, by growth from organometallic reagents in inverted micelles or in a hot coordinating solvent.^{1–4} In the synthesis method based on high-temperature solution chemistry, it has been shown that by controlling the initial preparation conditions, e.g., temperature and time of annealing, one can select the appropriate particle size and size distribution, thus allowing

several sizes to be made.^{2,3,14} Furthermore, because the capping molecules are weakly bound to the particle surface, it is possible to modify them (surface derivatization), allowing one to tailor the affinity of the crystallites to the surrounding solvent.^{19(a),20,21} The understanding of the interparticle interactions and their dependence on some relevant parameters. such as nature and size of the cap and solvent, is important. It allows one to better control the thermodynamic properties of these dispersions, and can be used for post synthesis analysis and processing of these materials. For instance, one should address whether or not the interactions in these systems behave like those in dispersions of conventional colloidal particles capped with polymer chains. Does the stability of these dispersions and the presence of a macroscopic colloidal order at high concentrations depend on how the interactions are affected by the capping groups? The solution properties of these semiconductor nanocrystals have so far received little attention, however.19

We previously reported a preliminary characterization of CdSe nanocrystal dispersions, where a few aspects of the interparticle interactions have been investigated.²² In this contribution, we report further investigation of these dispersions using small-angle scattering. We scanned a wide range of sizes and used several types of caps and solvents. The present study permits us to probe changes in the interactions as one or more relevant parameters are varied, in addition to providing accurate measure of the size and size distribution

7850

of the particles. Association (and aggregation) of particles in solvents, where strongly attractive interactions take place, can be observed. For dispersions where interactions are weakly attractive, existence of "dimers" in very small fractions is detected. Interparticle interactions may also depend on the size and the presence of excess free caps in the solution, for the smaller crystallites. These features imply that "dimerization" and binding of the capping units to the surface atoms are dynamic processes. They are influenced by the concentration as well as the excess of free caps. The features observed for the interactions are compared to theoretical approaches, such as the model of adhesive spheres and the concepts of steric stabilization, as done for colloidal dispersions.

We start with a description of the small-angle x-ray scattering (SAXS) technique and the concepts used in the data analysis. We then briefly describe the experimental setup and the materials preparation in Sec. II. In Sec. III, we present the SAXS spectra and their analysis. We then discuss the data and compare them to theoretical considerations without and with interactions, in Sec. IV.

II. GENERALITIES: THEORETICAL CONCEPTS

Inhomogeneous media, e.g., dispersions of solid particles and heterogeneous solids, are characterized by concentration fluctuations. They scatter electromagnetic radiation such as light or x ray. With x ray, the scattered signal is caused by electron density fluctuations in the medium. For a sample made of separate objects dispersed in a solution (e.g., a colloidal dispersion), the excess in the scattered intensity with respect to the solvent is a function of the electronic contrast between the solute objects and the solvent: $\Delta \rho = \rho_d - \rho_r$; ρ_d is the electron density per unit volume of the objects (quantum dots in this case) and ρ_r is the solvent (reference) electron density. For an isotropic sample, this intensity may be expressed as^{23–27}

$$I(q) = \int \Delta \tilde{\rho}^2(r) \left\{ \frac{\sin(qr)}{qr} \right\} 4 \pi r^2 dr$$
$$= \int 4 \pi p(r) \left\{ \frac{\sin(qr)}{qr} \right\} dr, \qquad (1)$$

where q is the scattering wave vector, $q = (4 \pi/\lambda) \sin \theta$, λ is the incident wavelength, and 2θ is the scattering angle; $\Delta \tilde{\rho}^2(r)$ is the autocorrelation function of the electronic contrast.^{23–27} The integration is carried out over all scattering elements in the irradiated volume V. We introduced the pairdistance distribution function defined as $p(r) = r^2 \Delta \tilde{\rho}^2(r)$.^{23–25} Equation (1) implies that p(r) may be evaluated from the inverse of the intensity using^{23–26}

$$p(r) = \frac{1}{2\pi^2} \int_0^\infty I(q) qr \, \sin(qr) dq.$$
 (2)

For the most general case, the scattered signal results from intraparticle and interparticle contributions, form factor P(q) and structure factor S(q), respectively,

$$I(q) = P(q) \times S(q). \tag{3}$$

However, one can reduce the intensity to contributions from one term or the other. For example, scanning small volume fractions ($\phi \rightarrow 0$), or using an "ideal" solution of noninteracting objects, permits us to substantially reduce S(q), and contributions from P(q) dominate the signal. We now discuss the cases without and with interactions.

A. Case without interactions

The problem is reduced to addressing the scattering properties of an individual object, since the total signal is a superposition of single-particle scattering $I_1(q)$: $I(q) \cong P(q) \sim NI_1(q)$, where N is the number of particles in the volume V. We now discuss a few features that emerge from the above expressions, which will be used in the analysis.

The extrapolation at q=0 provides the area under the function p(r) in real space, thus the total contrast of the scattering objects

$$I(0) = \int_0^\infty 4\pi p(r)dr = \int_0^\infty 4\pi r^2 \Delta \tilde{\rho}^2(r)dr = N(v\langle \Delta \rho \rangle)^2,$$
(4)

where v is the particle specific volume. For small ϕ , I(0,c) $\propto \phi$ or c (with $\phi = Nv/V$ and the concentration $c = d_s \phi$, where d_s is the mass per unit volume of the nanocrystals). I(q=0) is extracted from extrapolation at q=0, $I(0) \cong \lim_{a\to 0} \{I(q)\}$; it is not a directly measured value.

By expanding the sine in the integral [Eq. (1)] at small to intermediate q, following Guinier analysis, estimate for the particle size can be reached from

$$I(q,c) \cong I(0,c) \exp\left(-\frac{q^2 R_g^2}{3}\right)$$
 Guinier form, (5)

valid for qr < 1. The radius of gyration R_g has a modeldependent relation to the size and shape of the solute objects.^{23,24} For instance, $R_g^2 = (3/5)R_G^2$ for spheres of radius R_G (Guinier radius). A plot of $\ln(I)$ vs q^2 shows a linear behavior with a slope= $R_G^2/5$.

The integral of $q^2 I(q)$ over the whole reciprocal space is an *invariant*, Q proportional to the mean square of the electronic density fluctuations, but is independent of the subtle structure of the electronic contrast:

$$Q = \int q^2 I(q) dq = 2\pi^2 \Delta \tilde{\rho}^2(0) = 2\pi^2 V \phi(1-\phi) \langle (\Delta \rho)^2 \rangle.$$
(6)

For a set of noninteracting, or weakly interacting, particles Q becomes the sum of single-particle contributions: $Q \cong 2\pi^2 Nv \langle (\Delta \rho)^2 \rangle \cong NQ_1$, i.e., $Q \propto c$ or ϕ in dilute media $(\phi \ll 1)$. For homogeneous scattering particles, $\langle (\Delta \rho)^2 \rangle_v = (\langle \Delta \rho \rangle_v)^2$, and Eqs. (4) and (6) may be combined to provide a measure of the particle radius R_v (volume average size):²³⁻²⁶

$$\frac{2\pi^2 I(0)}{Q} = v = \frac{4}{3}\pi R_v^3. \tag{7}$$

Examination of the intensity at intermediate and large q can also provide information about the solute material. At large q (i.e., probing small r), one can write a linear expan-

sion for $\Delta \tilde{\rho}^2(r)$ at small r: $\Delta \tilde{\rho}^2(r) \approx \Delta \tilde{\rho}^2(0) \{1 - (s/4V)r + \cdots\}$, where *s* is the solute object's surface.^{23,24} Integration of Eq. (1) results in damped oscillations, with an average that decays as a power series of *q*. The first of that series is q^{-4} :^{23,24}

$$\lim I(q)_{q \ge 0} \cong \langle (\Delta \rho)^2 \rangle \, \frac{2\pi S}{q^4}. \tag{8}$$

S is the total surface of the scattering elements. A plot of $q^4I(q)$ vs q would start from zero at q=0, followed by damped oscillations averaged by a plateau that depends on $\Delta\rho$ and *S*. The periodicity of the curve depends on the size. For a narrow distribution the first maximum (at q_{max}) provides a measure of the radius: $R_M \cong 2.75/q_{\text{max}}$.^{23,24}

In reality the particles are always subject to a distribution in size, and one has to take that into account in the analysis. A few distribution functions are widely used to describe the polydispersity factor.^{22,29} We will limit our present analysis to the cases of log-normal and Gaussian distribution functions.

(i) For a log-normal function, the fraction of particles N(R) with a size laying between R and R + dR is given by²⁹

$$N(R)dR = NP_{\ln}(R)dR$$
$$= \frac{N}{\sqrt{2\pi}R\sigma_{\ln}}\exp\left\{-\frac{1}{2\sigma_{\ln}^{2}}\left[\ln\left(\frac{R}{R_{0}}\right)\right]^{2}\right\}dR, \quad (9)$$

where $P_{\ln}(R)$ is the probability to find a size R, σ_{\ln} is the standard deviation of $\ln R$, $\sigma_{\ln}^2 = \langle (\ln R - \ln R_0)^2 \rangle$, and R_0 is the geometric mean size: $\langle \ln R \rangle = \ln R_0$. The *n*th moment of the size can be expressed as $\langle R^n \rangle \cong R_0^n \exp([n^2 \sigma_{\ln}^2]/2)$. For small $\sigma_{\ln v}$ the variance is $v = \{\langle (R - \langle R \rangle)^2 \rangle\} \cong \langle R \rangle^2 \{ \exp(\sigma_{\ln}^2) - 1 \}$, the polydispersity, defined as $p = v^{1/2} / \langle R \rangle$, becomes $p \cong \sigma_{\ln v}$ and the full width at half maximum (FWHM) of the distribution is $\Delta R \cong 2.4 \sigma_{\ln} R_0$. From $\langle R^n \rangle$ one can derive these relations: $R_G = \{\langle R^8 \rangle / \langle R^6 \rangle\}^{1/2} \cong R_0 \exp(7\sigma_{\ln}^2)$, $R_v = \{\langle R^6 \rangle / \langle R^3 \rangle\}^{1/3} \cong R_0 \exp(4.5\sigma_{\ln}^2)$, and $R_M \cong R_0 \exp(3.4\sigma_{\ln}^2)$. A combination of two of the above relations provides preliminary values for R_0 and σ_{\ln} . These values are used to fit the intensity to theory over a wide range of q.

(ii) If the particles are described by a Gaussian distribution, N(R) becomes^{28,29}

Ν

$$(R)dR = NP_G(R)dR$$

= $\frac{N}{\sqrt{2\pi\sigma_G}R_0^G} \exp\left\{-\frac{(R-R_0^G)^2}{2(\sigma_G R_0^G)^2}\right\}dR.$ (10)

In Eq. (10), we use a "size normalized standard deviation," for consistency, where R_0^G is the mean size and $P_G(R)$ is the probability to find a size R. For small $\sigma_G \langle R \rangle = R_0^G$ and $p = (v)^{1/2}/R_0^G \cong \sigma_G$. Also, relations between the different moments of $\langle R^n \rangle$, R_0^G , and σ_G can be derived. For example, $R_G \cong R_0^G \exp(6.5\sigma_G^2)$, $R_M \cong R_0^G \exp(3\sigma_G^2)$, $\Delta R \cong 2.35\sigma_G R_0^G$, and $\sigma_G \cong (\ln[R_G/R_M]/3.5)^{1/2}$. $\sigma_{\rm ln}$ is equivalent to σ_G even though R_0 is not equal to R_0^G . We will show that the choice of the type of distribution function, log normal or Gaussian, is not crucial for small $\sigma_{\rm ln}$ or σ_G .

B. Case with interactions

In a medium characterized by isotropic correlations, the scattered intensity $becomes^{23-29}$

$$I(q,c) \cong NI_1(q) \left\{ 1 + \frac{N}{V} \int 4\pi r^2 [g(r) - 1] \frac{\sin qr}{qr} dr \right\}.$$
(11)

The term between brackets [equal to S(q) in Eq. (3)] accounts for the interparticle interactions; $V/N = v_1$ is the volume available for each particle. The correlation function obeys the conditions g(r)=0 for r<2R and $g(r)\rightarrow 1$ for $r \rightarrow \infty$.^{24,30} For distances close to R, $r=2R+\delta r$, g(r) is a function of the interaction potential V(r): $g(r) \cong \exp(-V(r))$.³⁰ Equation (11) for the intensity infers that S(q) is a "correction" to the form factor, which effects are most visible near q=0. A common form for the interparticle contributions is written in terms of the osmotic compressibility, $\chi_T = [1/c(\partial c/\partial \Pi)_T]$, using the following approximate expression for small c:

$$I(q,c) \cong KcM[I_1(q)\chi_T(q,c)].$$
(12)

K is a constant that depends on $\Delta \rho$, M is the particle mass, and Π is the osmotic pressure. Equation (12) can also be expressed in terms of the second virial coefficient A_2 :

$$I(q,c) \cong KcMI_{1}(q)[1 - 2A_{2}MQ(q,c)c].$$
(13)

Q(q,c) is an interference term that can be important for finite q and c.³¹ Limited to small c and q, $Q(q \rightarrow 0, c \rightarrow 0)$ $\rightarrow 1$, and one may write $I(q,c) \cong KcMI_1(q)[1 - 2A_2\phi d_s M]$.³¹ In a medium where interactions are repulsive A_2 is positive ($A_2 > 0$ and S(0) < 1), resulting in a negative contribution near q=0. A convex curvature of the intensity near q=0 is observed in a Guinier plot or a $\ln(I)$ vs q plot. This correction becomes positive for $A_2 < 0$ (attractive interactions: S(0) > 1) and a concave curvature is observed. In particular, for a hard sphere interaction potential, $g(r \le 2R) \equiv 0$, $g(r > 2R) \equiv 1$, and $S(q=0) \cong 1 - 8\phi$. A negative contribution to the intensity near the origin is then obtained.^{23,24,28-30}

Different models have been developed to describe media with attractive interactions. We consider the adhesive sphere model, initially formulated by Baxter, where he used the Percus-Yevick approximate equation for the radial correlation function for hard spheres.^{32–34} Regnault and Ravey built on that model and used a square potential well to predict the thermodynamic properties of colloidal dispersions:³⁵

 $V_A(r)/k_BT = \infty$ for $r \le 2R$ (*R* being the core radius), (14a)

$$V_A(r)/k_B T = \ln[12\tau(2\delta - 2R)/2\delta]$$
 for $2R < r \le 2\delta$,
(14b)

$$V_A(r)/k_B T = 0$$
 for $r > 2\delta$. (14c)

 $2\delta - 2R$ is the extent of the attractive square well, and τ is equivalent to a dimensionless temperature. It measures the degree of "adhesion" between particles. The case $\tau \rightarrow \infty$ cor-

Cap	Nanocrystal: λ_M (nm)	Solvents	Interactions, Stability	
TOP/TOPO	600, 564, 550, 540, 520	hexane, toluene	repulsive, stable	
TOP/TOPO	510, 482, 476, 472	hexane, toluene	weakly attractive,	
			stable	
TBP/TBPO	621, 562, 476	hexane, toluene	weakly attractive,	
			stable	
PYR	560	pyridine	weakly attractive,	
			stable	
PYR	550	toluene	attractive, unstable	
PIC	586	butanol	weakly attractive,	
			stable	

TABLE I. Materials studied: nanocrystals, caps, solvents, interactions, and stability conditions.

responds to the hard-sphere potential. We simply recall that the calculation provides the following form for $S(q=0,\phi < 1)$:

$$S(0) = \frac{1}{1 - C_{2\delta}(0)},\tag{15}$$

where $C_{2\delta}(q=0) \cong C_{2R}(q=0) + 2 \phi/\tau + (15/\tau - 3/\tau^2 + 1/6\tau^3)\phi^2 + 0(\phi^3)$; $C_{2R}(q=0)$ is the hard-sphere value. $S(0) \cong Nk_B T \chi_T$; it is related to the phase diagram of the medium. In particular, there is a critical point with the coordinate: $\tau_c \cong 0.0976$ and $\phi_c \cong 0.12$. For $\tau > \tau_c$ a single domain exists, whereas for $\tau < \tau_c$ phase separation occurs. In the above considerations, the structure factor depends on the product $\tau \phi$.^{33,35} Consequently, substantial effects on S(q) and the phase diagram may be seen only at larger concentrations.

The analysis is carried out as follows. We first compare the data to theoretical fits using a distribution of noninteracting spheres over a wide range of q, but not in the immediate vicinity of q=0. From the fit, we extract estimates for R_0 and p (or σ). Comparison of the data and fit near q=0 in a Guinier or $\ln(I)$ vs q plots provides information about the interactions. A positive departure of the intensity with respect to the fit near q=0 in either plot accounts for attractive interactions. However, a negative departure from the fit reflects dominance of repulsive stabilizing interactions. Second, stable dispersions are compared (briefly) to the predictions of the hard-sphere model. We compare the data with negative correction to the model of adhesive sphere potential, and to fits using two distributions of particles, monomers, and "dimers." Last, we compare the data to the concepts of steric stabilization, with emphasis on the effects of cap density and affinity to the solvent, their lateral extension, and nanocrystal size.

III. EXPERIMENTAL SECTION

A. SAXS setup

The x-ray source is a rotating copper anode (Rigaku) operated at 40 kV and 25 mA. The apparent point source is about 10^{-2} mm². A curved mirror made of gold coated quartz, placed after the source, eliminates the higher energy photons and reflects the copper wavelengths $\lambda_{Cuk\alpha}$ and $\lambda_{Cuk\beta}$. It also collimates the beam onto a position-sensitive detector, PSPE (Elphyse), with a 3 or 4 mm height window, a useful length of 50 mm, and a resolution of 200 μ m. A thin vertical slit, placed after the mirror, selects a rectangular beam with the dimensions of $3 \times 0.3 \text{ mm}^2$ on the detector. A nickel filter after the slit eliminates the wavelength $\lambda_{Cuk\beta}$, allowing one to select a monochromatic beam at $\lambda_{Cuk\alpha}$ = 1.54 Å. This setup permits us to scan a *q* range between $6 \times 10^{-3} \text{ Å}^{-1}$ and 0.4 Å⁻¹, with a resolution of $3 \times 10^{-3} \text{ Å}^{-1}$. Experimentally, we collect the signal from the reference, I_{ref} then from the sample, I_s . The difference $I = I_s - I_{\text{ref}}$ is used in the analysis.

B. Materials and sample preparation

The CdSe nanocrystals used in the present study are made from organometallic precursors, nucleation, growth, and ana hot (300–340 °C) nealing in a hot $(300-340 \ ^\circ\text{C})$ coordinating solvent.^{2,4,10,11,18,19} Temperature is an important controlling parameter. Size-selective precipitation, carried out two to three times after synthesis, permits us to isolate nanocrystals capped with a mixture of trioctyl phosphine and tryoctyl phosphine oxide (TOP/TOPO), and further narrows the size distribution. The capping units can be exchanged, allowing one the ability to modify the electronic properties of the surface and to tailor the crystallite compatibility with a vari-ety of solvents.^{2,4,19,21} The cap exchange is achieved by exposing the initial dots to an excess of competing capping groups.^{2,4,19,21} Addition of a solvent compatible with the initial caps but not with the new ones results in flocculation of particles capped with the new groups. Repeating this operation two or three times provides a nearly complete cap exchange (>95%) as verified by ¹³C NMR.²¹ Cap exchange offers the opportunity of exploring the dependence of the interactions on the properties of the dot's surface and the solvent. In the present study, we explored four types of capping groups (Table I). The first is made of TOP/TOPO molecules. The second are pyridine (PYR) molecules; they are attached to the surface in an exchange reaction by dissolving the initial dots (with TOP/TOPO) in pyridine. We performed only one dissolution in pyridine, but anticipated a high rate of cap exchange, because a small amount of nanocrystals was used (c < 0.5%). In addition, given the strength of the reaction, the cap exchange is associated with a slight erosion of the crystallite surface (about 3–5 % loss in size). The third type is a mixture of tributyl phosphine and tributyl phosphine



FIG. 1. uv-visible absorption and photoluminescence spectra for a dispersion of 586-TOP/TOPO capped particles in hexane. The arrow indicates the position of the first absorption peak at λ_M .

oxide (TBP/TBPO). The fourth type are picoline (PIC) molecules. Along with these, we explored four types of solvents. Hexane and toluene are used to disperse crystallites capped with TOP/TOPO and TBP/TBPO. Pyridine and toluene are used to disperse PYR capped dots. Butanol is used to disperse PIC capped particles. uv-visible absorption spectra were taken before and after measurements. No changes were observed. We identify the sample with the location of its first absorption peak and the type of cap (Fig. 1), e.g., samples 586-TOP/TOPO or 586-PYR correspond to nanocrystals with a band-edge absorption at $\lambda_M \approx 586$ nm and capped with TOP/TOPO or PYR groups, respectively. Given the high electronic density of the Cd and Se with respect to the solvent and caps, the scattered signal results primarily from the inorganic core. This permitted the use of small concentrations to achieve high signal-to-noise ratios. Samples are quartz capillary tubes, with ~ 1 mm optical path, filled with the desired dispersion. They are flame-sealed after filling to avoid contamination and evaporation of the solvent.

IV. RESULTS

Intensity spectra invariant Q

Figure 2 shows the total scattered (SAXS) intensity ($I_{tot} = I_{dots} + I_{solvent}$) for a few dispersions (with different concentrations) of 550-TOP/TOPO in hexane. These spectra show a classic behavior with a large contribution from the solute nanocrystals at small angles, and a decrease to zero as q increases. The large contribution to the signal in the small q regime results from the high electron density of the nanocrystals. Similar behavior is observed with the other dispersions, except for PYR capped dots in toluene where a weak signal is collected. These dispersions (PYR capped in toluene) show a macroscopic precipitation.

The intensity extrapolated at the origin, I(0), for dispersions of TOP/TOPO and PYR capped dots in hexane and pyridine, respectively, increases linearly with concentration: $I(0,c_1)/I(0,c_2) = c_1/c_2$ (inset in Fig. 2 and Table II). This result is in agreement with the predictions discussed in Sec. II. No concentration scan was carried out for dispersions of PIC capped crystallites. The scan carried out for dispersions of PYR capped dots in toluene did not provide useful information because of the precipitation.

Figure 3 shows experimental curves for $q^2I(q)$ vs q [Eq. (6)] for dispersions of 550-TOP/TOPO in hexane and 560-PYR in pyridine, respectively. The corresponding invariant Q increases linearly with concentration as anticipated (see Table II and the inset in Fig. 3). From the values of Q and I(0) we extract an estimate for R_v using Eq. (7). Analysis was limited to stable dispersions, i.e., TOP/TOPO capped nanocrystals in hexane and toluene, TBP/TBPO dots in hexane, and PYR capped nanocrystals in pyridine. Similar values are measured for comparable crystallites (same λ_M), independent of the cap used.



FIG. 2. Total scattered intensity for a few dispersions of 550-TOP/TOPO nanocrystals dispersed in hexane along with the pure solvent reference. The inset shows the linear dependence of I(0) vs c for dispersions of 550-TOP/TOPO in hexane (\blacksquare) and 560-PYR in pyridine (\blacktriangle). The coincidence of the respective data for both sets of dispersions is due to the close size of the nanocrystals.

TABLE II. Invariants, Q I(0), and size measurements for the samples used. The variation of I(0) and Q from one sample to another is due to variation in the concentration.

Sample identification	$Q(q_M \simeq 0.3 \text{ Å})$	<i>I</i> (0) (a.u.)	$R_v(\text{\AA}) \simeq [3 \pi I(0)/2Q]^{1/3}$	R_0 (Å)	R_G (Å)
550-TOP/TOPO in hexane, $c \simeq 1.75\%$	10.9	17791	19.7	19.3	22.3
550-TOP/TOPO in hexane, $c \approx 0.93\%$	5.64	9520	19.9	19.2	22.4
550-TOP/TOPO in hexane, $c \approx 0.285\%$	2.005	3577	20.3		
550-TOP/TOPO in hexane, $c \simeq 0.26\%$	1.625	3161	20.9		
560-PYR in pyridine, $c \simeq 0.47\%$	2.94	4225	18.9	19.7	22.8
560-PYR in pyridine, $c \approx 0.35\%$	2.4	3552	19.1	19.7	22.8
560-PYR in pyridine, $c \approx 0.28\%$	1.557	2470	19.55	19.8	22.8
560-PYR in pyridine, $c \simeq 0.235\%$	1.38	2077	19.2		
600-TOP/TOPO in hexane	0.408	1715	25.2	24.9	29.5
564-TOP/TOPO in hexane	1.469	3286	21.9	21.3	23.8
540-TOP/TOPO in hexane	0.978	1606	19.7	18.8	21
520-TOP/TOPO in hexane	1.517	2172	18.8	17.4	19.5
510-TOP/TOPO in hexane	0.750	723	16.5	14.5	18.5
564-TOP/TOPO in toluene	1.332	2829	21.5	21.5	24
540-TOP/TOPO in toluene	0.828	1256	19.25	18.8	21.2
622-TBP/TBPO in hexane	2.165	11700	29.4	29.7	34.5
562-TBP/TBPO in hexane	1.30	2580	21	20.6	23.7
586-PIC in butanol				22	24.5



FIG. 3. Plots of $q^2 I(q)$ vs q for dispersions of 550-TOP/TOPO in hexane at three concentrations, and for 560-PYR in pyridine. The invariant is obtained from the integration of the above curves over the whole range of q. The inset shows the linear dependence of Q on c for dispersions of 550-TOP/TOPO (\blacksquare) in hexane and 560-PYR in pyridine (\blacktriangle). The coincidence of the experimental invariant for both sets of dispersions is due to the close size of the nanocrystals.

Guinier diagrams

In Fig. 4, we show Guinier plots $[\ln(I) \text{ vs } q^2]$ for a few dispersions studied: TOP/TOPO capped in hexane, TOP/TOPO capped in toluene, PYR capped in pyridine, PYR capped in toluene, and TBP/TBPO capped in hexane.



FIG. 4. Guinier plots for different dispersions. Some of the spectra are multiplied by a scaling factor to avoid overlapping. The curvature near the origin with respect to a linear fit varies with the pair cap solvent used.



FIG. 5. Guinier plots $\ln(I)$ vs $(qR)^2$ for various size TOP/TOPO capped crystallites dispersed in hexane (top) and in toluene (bottom). Some of the spectra are multiplied by a scaling factor to avoid overlapping. A change in the curvature near q=0 from convex to concave is observed when the size decreases below ~ 15–16 Å in either case. Values of λ_M (nm) and R_0 are given.

All diagrams show a linear regime for small to intermediate q (Guinier behavior), as predicted by Eq. (5). However, the type of curvature near the origin, with respect to a straight line, depends on the pair cap-solvent used. For example, data from dispersions of TOP/TOPO capped particles showed a convex curvature in hexane and toluene, reflecting the presence of repulsive stabilizing interactions. PYR capped dots dispersed in pyridine showed a concave curvature near q=0, however. The negative curvature becomes more pronounced when PYR capped dots are dispersed in toluene, which reflects the presence of strong destabilizing attractions between nanocrystals. The data from TBP/TBPO and PIC capped dots dispersed in hexane and butanol, respectively, show a behavior similar to that observed for PYR capped nanocrystals in pyridine. From the linear region in the above plots, we extract values for the Guinier radius R_G (see Table II). Similar values are deduced for nanocrystals with similar λ_M , independent of the type of caps and interactions.

Remark. Effects of temperature on the above spectra could not be explored in "extensive" details. Only measurements at temperatures below 65 °C were attempted, because of the solvents low boiling temperatures. No effects were observed.

Nevertheless, the data from dispersions of alkyl (TOP/ TOPO) capped nanocrystals do not automatically show re-



FIG. 6. Guinier diagrams for dispersions of 510-TOP/TOPO nanocrystals ($R_0 \cong 14.5$ Å) in hexane, with various concentrations of excess free cap, c_p . The free caps are made of a mixture (50% TOP and 50% TOPO). The concave curvature near q=0 decreases and is suppressed as c_p increases.

pulsive interactions, namely a convex curvature near q=0, independent of the size. Figures 5(a) and 5(b) show the experimental plots for $\ln(I)$ vs $(qR)^2$ (with $qR \le 2$) for various sizes TOP/TOPO capped nanocrystals dispersed in hexane and in toluene. A plot of $\ln(I)$ vs $(qR)^2$ (instead of q^2) ensures that comparison between the data for different sizes is carried out at comparable Guinier domains.²³ The interactions (reflected in the curvature near q=0) are reversed from repulsive to attractive when the size decreases below a "critical" value of ~15–16 Å. Such behavior is unexpected for colloidal materials.^{36,37} It can result in macroscopic precipitation of the solutions for smaller sizes after excessive "washing" (several size selections). It is also in agreement with luminescence data where smaller quantum yield is measured for the smaller particles.¹⁹

To better understand the behavior of dispersions with smaller TOP/TOPO capped particles, we probed changes of the interactions in the presence of excess free caps at fixed concentration (titration with free caps). Figure 6 shows representative Guinier diagrams for dispersions of 510-TOP/TOPO in hexane with various amounts of free caps, c_n (made of 50:50 TOP:TOPO). The concave curvature near q=0, present at $c_n=0$, is progressively reduced and disappears as c_p increases. This gradual change results from a progressive reduction of the attractions, and their eventual inversion, when c_n is increased. The change in the curvature near q=0 reaches an asymptotic limit, followed by the appearance of a nonzero background at large q. This reflects the appearance of micelles of TOP and TOPO in the medium. These micelles result from a thermodynamic equilibrium in the solution between the particle surface and free caps. For the polar heads of the caps, there are two favorable "states" with higher electronic activity: on the nanocrystal surface or within independent micelles. The latter state is reached only at high c_p .

Porod analysis

In Fig. 7 we show representative Porod plots, $q^4I(q)$ vs q, for a few dispersions studied, e.g., 550-TOP/TOPO in hex-



FIG. 7. Few typical Porod plots for the dispersions studied. 550-TOP/TOP in hexane at three different concentrations (top); data for other solutions with weaker intensity, 622TBP/TBPO in hexane, 564-TOP/TOPO in toluene, and 562-TBP/TBPO in hexane (bottom). The intensity is multiplied by 5 for the three bottom samples. The arrows indicate the positions of $q_{\rm max}$, which moves to lower values for larger size.

ane or toluene, 622-TBP/TBPO in hexane, and 564-TOP/TOPO in toluene. These plots are similar to classical Porod diagrams reported for colloidal particles, e.g., dispersions of calcium sulfonate in oil and carbonate particles in reverse microemulsions, with zero intensity at the origin and a peak at q_{\max} , followed by oscillating scattered intensity.^{23–27,36,37} The scattering in the data at larger q is due to lower signal-to-noise ratio. The location of q_{max} is identical for particles with similar λ_M , independent of the cap and solvent. From R_G and R_M we extract preliminary values for R_0 and σ_{\ln} (or R_0^G and σ_G), which are then used to generate fits to the data. We use Porod diagrams to fit the data to intensity derived from a set of noninteracting polydisperse spheres, over a wide range of q around the first peak, but not including the region very near q = 0. The use of a population of noninteracting spheres is justified since the region near q=0 (where contributions of the interactions are present) is discarded. Using Porod analysis provides a more accurate estimate for R_0 and σ_{ln} since a fit to a peak is involved, in comparison to simply fitting the intensity (e.g., in Fig. 2).^{22–27,36,37} In the above fits we considered both types of distributions, log normal and Gaussian (see Fig. 8). We found that the value extracted for R_0 and p are very close in either case. In the following we limit the discussion to lognormal distribution. The above generated theoretical curves are then compared to experiment over the full range of q. Such comparison is better reflected in Guinier (Fig. 4) and $\ln(I)$ vs q plots,²² with a positive or negative departure be-



FIG. 8. Experimental data together with fits to a population of noninteracting spheres, using either log-normal or Gaussian distributions for a dispersion of 550-TOP/TOPO in hexane. Porod (top) and ln(*I*) vs *q* (bottom) plots are shown. Very close values are found for either fit: $R_0 \cong 19.30$ Å and $\sigma_{ln} \cong 0.113$ while $R_0^G \cong 19.25$ Å and $\sigma_G \cong 0.115$. Arrows indicate the lower and upper limits of the fit.

tween experiment and fits near q=0, for attractive and repulsive interactions, respectively.

Pair-distance distribution function: p(r)

Figure 9 shows three typical experimental curves for qI(q) vs q and the corresponding pair-distance distribution function p(r), extracted from the above curves via a sinus Fourier transform [Eq. (2)]. This Fourier transform requires extrapolation near q=0 with the assumption $I(q) \propto q^2$. It also requires an extrapolation at large q, where $I(q) \sim 1/q^4$ is assumed.^{23–27} The curves of qI(q) vs q are less symmetric for PYR capped particles in pyridine and toluene than for dispersions of TOP/TOPO capped particles. p(r) has a symmetric peak at $r_p \approx 20.5$ Å for dispersions of 550-TOP/TOPO in hexane. The position of the peak is very close to what is predicted for spherical particles in stable dispersions with size R_0 ($r_p \approx 1.05R_0$). However, p(r) is less symmetric for 560-PYR in pyridine, with two disproportionate peaks. The first is located at $r_{p1} \approx 21$ Å and the second is at $r_{p2} \approx 53$ Å. This may reflect the existence of two populations, monomers and "dimers," with disproportionate fractions, in agreement with Guinier and Porod analyses (see the discussion below). The data from 550-PYR capped particles dispersed in toluene showed a more complex behavior with one peak located at $r_p \sim 20.3$ Å, similar to what is observed



FIG. 9. Experimental data for qI(q) vs q for the three types of solution (top); the corresponding pair-distance distribution function p(r) (bottom). The data for p(r) are multiplied by scaling factors, i.e., 560-PYR in pyridine by 3 and 550-PYR in toluene by 5. Three different behaviors are reflected in p(r): single population, mixture of monomers and "dimers," and aggregates. Arrows indicate the peak locations for populations of single particles for the different samples.

for 550-TOP/TOPO, and a broad second peak made of several "subpeaks" with various intensities. This may reflect the existence of several populations, monomers (with small fractions) coexisting with various size aggregates, e.g., "dimers," "trimers," etc. This picture is *a priori* incomplete, because of the macroscopic precipitation, where the larger aggregates precipitate in the bottom of the capillary, and do not contribute to the signal.

Close-packed precipitates

We also explored the effects of adding various amounts of nonsolvent (ethanol in this case) to dispersions of 550-TOP/TOPO and 564-TOP/TOPO in hexane, in order to probe the influence of varying the solvent quality on the interactions. The Guinier diagrams from these samples show that interactions (convex curvature) are changed only after the mixture hexane:ethanol exceeds a ratio of ~1:4. Precipitation of the particles follows shortly after. We performed SAXS measurements on precipitates of those dispersions with a larger amount of ethanol (ratio ~1:10). The spectrum is very different from what is observed in Fig. 2. It shows a very low signal at small q, and a well-defined peak at q_p ,



FIG. 10. SAXS spectra from a close-packed sample, prepared from precipitating out an initial dispersion of 564-TOP/TOPO in hexane with a large excess of ethanol. The center-to-center distance is deduced from the position of the peak, $D = (1.5)^{1/2} D_{\text{Bragg}} \approx (1.5)^{1/2} 2 \pi/q_p$.

located at 0.141 and 0.1306 Å⁻¹ for 550-TOP/TOPO and 564-TOP/TOPO, respectively (Fig. 10). We attribute this to the presence of close-packed particles in these aggregates. The average core to core separation in these close-packed structures is given by $D \cong (1.5)^{1/2} D_{\text{Bragg}} \cong (1.5)^{1/2} D(111)$.³⁸ This provides a distance $D \cong (1.5)^{1/2} 2 \pi/q_p \approx 54.5$ and ≈ 58.5 Å for 550-TOP/TOPO and 564-TOP/TOPO nanocrystals, respectively. The difference between D/2 and R_0 ($\sim 7-8$ Å) is due to the capping groups on the nanocrystal surface.

V. DISCUSSION

Size and size distribution, comparison with other measurements

The linear increase of I(q=0) and Q with concentration, for TOP/TOPO and PYR capped crystallites, is in agreement with Eqs. (4) and (6). This confirms that when the interparticle contributions are reduced, the intensity results from P(q), which has a linear increase with concentration for small $c.^{23-27}$ The values shown in Table II for the different averages of the particle size are consistent. In particular, we find that R_0 and σ are in good agreement for dispersions with similar λ_M . This is independent of solvent, cap, type of interactions, and the distribution function, log normal or Gaussian, used in the analysis (see Fig. 8). We compare the present sizes to TEM data and to other SAXS experiments carried out over larger angles $(0.1 < q < 1 \text{ Å}^{-1})$. In both cases, "solid" samples of particles dispersed in a polymeric matrix have been used.¹⁹ Very good agreement between the two SAXS measurements is found. However, high-resolution TEM always provided smaller estimates for R_0 (2–3 Å) and σ . The discrepancy can be attributed to the high-resolution TEM lack of sensitivity to the amorphous atomic outer layers $(\sim 1 \text{ atomic layer near the particle surface})$, despite well rendering of the core crystallinity. Also smaller particle numbers are involved in estimating R_0 and σ . In the present measurements we could not account accurately for a small anisotropy (\sim 1.05 to 1.2 from small to larger size). This is primarily due to low signal-to-noise ratio at larger q in the present case, where well-defined oscillations in the intensity have not been reached. The anisotropy in shape may translate into a slightly larger σ with respect to TEM data. Poly-dispersity can be further reduced by performing additional size selection,^{19a} but at the expense of damaging the surface of the crystallites and reducing their solubility.

Because x-ray scattering is sensitive to $\Delta\rho$, the present sizes account only for the inorganic core in the nanocrystal. The caps, made of phosphor and hydrocarbon atoms, have an electron density similar to that of the solvent, but much smaller (~5 times smaller) than that of the core. However, the organic caps affect the dynamic size of a moving particle. We measured the hydrodynamic radius, R_H , for dilute dispersions of 550-TOP/TOPO in hexane, using quasielastic light scattering (QELS) at the krypton line $\lambda = 647$ nm, away from the absorption band of the nanocrystals. R_H is derived from the diffusion coefficient of the particle, *D*, using the Stokes relation,

$$R_H = \frac{1}{6\pi\eta_s D},\tag{16}$$

where η_s is the solvent viscosity. The size measured, R_H \approx 33 Å, is larger than R_G and R_0 , with $R_H \approx 1.7 R_0$. The difference between the two estimates can be attributed to two factors. First, we know that for dispersions of bare solid spheres, contribution from hydrodynamic interactions, accounted for using the Oseen tensor, results in an R_H larger than R_G and R_0 .³⁹ Second, those contributions are also sensitive to the full moving object, core plus shell, which would also result in a larger R_H compared to bare spheres. A quantitative account for the shell contributions is difficult, given their innate complex nature. Nevertheless, their presence is substantially reflected in the measure of R_H . Effects of the caps are also reflected in the SAXS spectra of close-packed nanocrystal aggregates dispersed in hexane and precipitated with an excess of ethanol. The difference between D/2 and R_0 accounts for the shell's lateral extension, L, but is only an approximate estimate of the cap size since these groups may interpenetrate in a close-packed structure. Nonetheless, the contributions of the shell to R_H prove that the caps do not collapse on the particle surface.

Interparticle interactions

The interparticle interactions (and the thermodynamic properties of these dispersions) are affected by two key parameters: pair solvent-cap and nanocrystal size. We distinguish three categories. The first category is made of dispersions characterized by repulsive interactions, and stable for a long time (years). They are made up of TOP/TOPO capped particles and dispersed in either toluene or hexane. Nevertheless, within this category there are limitations. Dispersions of particles with size below 15 Å show weak attractions that can become strong with excessive "washing." The second category is made of stable dispersions but characterized by weak attractions. This category includes PYR capped particles dispersed in pyridine, PIC capped nanocrystals dispersed in butanol, and crystallites capped with shorter alkyl molecules, TBP/TBPO, dispersed in hexane or toluene. In these media similar and consistent behavior is observed over



FIG. 11. Comparison between experimental data for 560-PYR in pyridine and fit using the model of adhesive spheres described in Sec. II.

the whole range of particle sizes. The third category is made of dispersions with strong attractions, where macroscopic precipitation is observed. They are PYR capped nanocrystals dispersed in toluene or in hexane.

For stable dispersions (category 1), we compared the difference at q=0 for dispersions of 550-TOP/TOPO in hexane to the prediction of the hard-sphere potential: $S(0) \cong 1$ -8ϕ ($A_2d_sM \cong 4$). The experimental "correction" in the above structure factor is slightly larger than the prediction. Furthermore, it does not show a clear linear dependence on concentration for the values scanned. This implies that a potential of hard spheres is not appropriate in describing the interactions in the present dispersions. The disagreement may be understood when considering the microscopic structure of the materials (inorganic core and a soft shell). The shell made of polar heads and alkyl chains results in a potential more complex than the one for hard spheres.

For stable dispersions but with attractive interactions, e.g., PYR and PIC capped particles in pyridine and butanol, respectively, the intensity can be fit to a set of polydisperse noninteracting spheres, but over a more reduced window of scattering angles (Figs. 11 and 12). The discrepancy between fit and data extends over a wider range of q than the case with TOP/TOPO capped nanocrystals.²² Furthermore, the difference between fit and experiment is not affected by concentration. The data for PYR capped crystallites in pyridine are compared to the predictions of the adhesive sphere model (see Fig. 11). We find that the predictions always underestimate the experimental contributions. A concave curvature near q = 0 in the fit can eventually be observed, but only with an unrealistic interaction parameter, i.e., $\tau^{-1} > 10.24$ (or τ $< \tau_c$); the present volume fractions are too small for any precipitation to occur.^{32,33,35} We attribute this failure to the inadequacy of the potential of adhesive spheres in describing the cap role. These groups have lateral extension (e.g., TBP/TBPO, PIC) compared to the sphere size. They also interact with the solvent. In the case of PYR caps, the shell is a natural extension of the solvent, and a potential well is not appropriate to describe the interactions.



FIG. 12. Comparison between experimental data for 560-PYR in pyridine and 586-PIC in butanol and fits using one and two populations of spheres. Single population: $R_0 \cong 19.7$ Å and $\sigma \cong 0.12$ for 560-PYR; $R_0 \cong 22$ Å and $\sigma \cong 0.1$ for 586-PIC. Two populations: $R_1 \cong 19$ Å, $\sigma_1 \cong 0.12$, $R_2 \cong 43$ Å, and $\sigma_2 \cong 0.2$, with 90% monomers and 10% "dimers" for 560-PYR; $R_1 \cong 21.2$ Å, $\sigma_1 \cong 0.1$, $R_2 \cong 61.5$ Å, and $\sigma_2 \cong 0.2$, with 87% monomers and 13% "dimers/trimers" for 586-PIC. Only a log-normal function is used in this case. A fit with two populations with disproportionate fractions is better; Guinier and $\ln(I)$ vs q (inset) plots are shown.

Because of the observed lack of dependence of the concave curvature near q=0 on c, we compare the above data (560-PYR and 586-PIC) to fits with two disproportionate populations, e.g., 85-90% monomers and 10-15% "dimers" (dimers are approximated by spheres). The values for R_1 and σ_1 (single population) and the values for R_0 and σ , deduced from the previous fit, are in agreement. The comparison between fit and experiment is shown in Guinier, and $\ln(I)$ vs q plots (Fig. 12). It accounts much better for the experimental data near q=0. The small population of "dimers" and the long-term stability of these dispersions may reflect the presence of a dynamic "dimerization" process. Two particles can come close because of the attractive potential. They stick to each other over a certain period of time and then dissociate while another "dimer" is formed. The difference between experiment and fit with polydisperse noninteracting spheres for 550-PYR in toluene could not be accounted for using two populations of monomers and "dimers." Furthermore, since these dispersions show macroscopic precipitation, various size aggregates are present, but only the small (floating) ones contribute to the signal.

Comparison to the concepts of steric stabilization

The presence of polymeric chains, grafted or adsorbed on the particle surface, is known to influence the thermodynamic properties of colloidal materials.²⁹ The treatment of steric stabilization was developed to address aspects of colloidal stability using polymeric materials. Extrapolation of that treatment to the present case is based on the similarity between (L/R_0) and the ratio between polymer lateral size to that of a colloidal particle. However, there are limitations to such comparison. The nanocrystals are nanometer size whereas most classical colloidal particles are about 10 to 500 times larger. Also the alkyl caps (e.g., TOP, TOPO, TBP, TBPO, PIC) are much smaller than the polymer chains used with classical colloids, e.g., polymer chains are 10 to 1000 times larger than these caps. Consequently, one must keep in mind these limitations when considering the forthcoming discussion.

The interaction potential in the treatment of steric stabilization is made of two separate (often competing) contributions: the van der Waals attractive potential between bare particles and the energy of mixing between shells and between shell and solvent. It is the second contribution that can impose steric stabilization on the dispersion, when it is positive and larger than the van der Waals term. The free energy of mixing between the shells and solvent is given by the Flory-Huggins equation for polymer solutions.^{39–43}

$$\Delta G^{M} = k_{B}T\{[n_{s}\ln(1-\phi_{c})+n_{c}\ln\phi_{c}]+n_{c}\phi_{c}\chi\}$$
$$\approx k_{B}T\{[n_{s}\ln(1-\phi)+n_{c}\ln\phi]+n_{c}\phi\chi\}.$$
 (17)

The first term in Eq. (17) is the combinatorial energy (entropy term) that accounts for the different possibilities of mixing polymer segments and solvent molecules. The second term is the contact dissimilarity contribution, with χ being the Flory interaction parameter.^{39–43} n_s and n_c are, respectively, the numbers of solvent molecules and polymer segments (or cap segments) in the mixing medium; ϕ_c is the volume fraction of the polymer segments (or capping segments) in that medium. Because of the proportionality between the volume fraction of the capping units and that of the colloids (constant surface coverage), we substitute ϕ_c by ϕ in Eq. (17). As two particles are brought in close contact, their shells progressively overlap. It is the sign and the magnitude of the free energy inside that overlapping domain (also known as interpenetrational domain) that defines the stability of the dispersion. For the sake of clarity, we first consider the above energy for two flat plates $\Delta G_{\rm FP}^{M}$ covered with polymeric brushes (or shells) of thickness L.²⁹ The change in energy for a very small volume δV in that stabilizer sheath (and for small ϕ) is

$$\delta(\Delta G_{\rm FP}^{M}) = (k_{B}T/V_{1}) \{ -(1-\chi)\phi + (\frac{1}{2}-\chi)\phi^{2} \} \delta V.$$
(18)

We ignored the terms higher than ϕ^2 in the Taylor expansion. This equation is valid for all domains of approach. Because of the plane symmetry, δV may be expressed as $\delta V = \Sigma \, \delta x$, where Σ is the plate surface and x is the lateral distance from that plate. Assuming constant density (both surface and lateral), the integration of the above energy over the volume of the two shells (two plates) yields

$$\Delta G_{\rm FP}^{M} = 4k_{B}T \left\{ \frac{V_{s}^{2}}{V_{1}} \right\} N^{2} \nu_{c}^{2} (\frac{1}{2} - \chi) \left(\frac{1}{L} - \frac{x}{2L^{2}} \right), \qquad (19)$$

where ν_c is the number of chain contacts (bonds) per unit area on the plate, N is the number of segments in a chain (or a capping group), and V_s and V_1 are the volumes per solute segment and solvent molecule, respectively. In Eq. (19), V_s and V_1 , respectively, result from the following expressions $\phi_c(\propto \phi) \cong \rho_s V_s$ and $\delta n_s = (1 - \phi)(\delta V/V_1)$. ρ_s is the the density of segments within a shell and δn_s is the number of solvent molecules in δV . The density ρ_s , assumed constant, is divided into a surface density that provides ν_c (after integration) and a linear lateral density (along *x*) expressed as $\rho_1 \cong 1/L$. The factor 4 is derived from integration and the use of two plates. The above free energy for two free plates can be extended to describe two spherical particles, ΔG_s^M , of finite radius R_0 , using the Deryaguin approximation:²⁹

$$\Delta G_s^M = \pi R_0 \int_{dm}^{2L} \Delta G_{\rm FP}^M \, dx, \qquad (20)$$

where d_m and d_M (~2L) are the respective minimum and maximum separation distances between the particles at which interactions take place. The resulting energy of mixing may then be expressed (after integration) as

$$\Delta G_{s}^{M} = \left[4 \pi R_{0} k_{B} T \left\{ \frac{(N \nu_{c} V_{s})^{2}}{V_{1}} \right\} (\frac{1}{2} - \chi) \left(1 - \frac{d_{m}}{2L} \right)^{2} \right].$$
(21)

On very close approach of the shells (spheres), another term describing interpenetrational-plus-compressional interactions adds to the free energy. That term has a positive sign and always favors repulsions, but will not be discussed here.²⁹ For a fixed size, the sign of the free energy depends on the Flory parameter, χ . This parameter describes the segment-monomer (solvent) interactions, and should not be strongly influenced by the cap extension. For $\chi > 0.5$, ΔG_s^M is negative. Interactions are attractive, and favor close approach between particles. The energy becomes positive for $\chi < 0.5$, favoring repulsions, thus stability of the dispersion. The above discussion is reminiscent of polymer solutions where $\chi = 0.5$ corresponds to θ solvent condition. The case $\chi < 0.5$ corresponds to good solvent condition for the shell, i.e., proximity of the cap to the solvent is favored, whereas χ >0.5 corresponds to poor solvent condition.^{39–43} The mag-nitude of the above mixing energy ΔG_s^M depends (strongly) on three characteristics of the capping sheaths: density of coverage per unit area, length of the caps, and volume per solute segment, ν_c , N, and V_s respectively. It also depends on the size, R_0 . Since the overall interaction energy is the superposition of ΔG_s^M above and the van der Waals core to core attractions, it is the magnitude of the mixing energy (when it is positive) that imparts thermodynamic stability on the dispersion. This is where the size (N), surface density (v_c) , and the volume per segment (V_s) intervene the most, because ΔG_s^M is proportional to the square of their product. We refer to this product as the "stabilizing parameter" of the capping shells. Within these considerations, one may distinguish three categories.

1. Sterically stabilized dispersions

They are primarily made of TOP/TOPO capped crystallites dispersed in hexane and in toluene. These caps have the largest lateral extension. An extended configuration permits more favorable contacts between the segments and the surrounding solvent molecules. If $\chi < 0.5$, ΔG_s^M is positive and large (large "stabilizing parameter," $N\nu_c V_s$); it can overcome the van der Waals attractions, resulting in a positive mixing energy. This favors repulsions between nanocrystals, thus stability.

The different behavior observed for dispersions of smaller size particles with TOP/TOPO caps can be understood within the framework of the above concepts. The inversion of the interactions when the particle size decreases is caused by a decrease in the mixing energy with respect to the van der Waals term, due to a smaller "stabilizing parameter" in ΔG_s^M . The primary cause for such a decrease is a lower surface density. In fact, we know that for very small nanocrystals a less "continuous" surface emerges.^{44,45} Only a limited number of sites are available for the caps to strongly bind to, resulting in lower cap coverage. In addition to the effects of surface density, a decrease in the particle size would also decrease the mixing energy as shown in Eq. (21). Last, smaller particles have higher surface curvature (i.e., larger area per cap), thus a weaker shielding of the core to core attractions. The overall potential of interactions would be attractive, but not strong enough to induce flocculation in the medium, unless excessive "washing" of the particle surface is carried out. The above considerations are in agreement with the study performed on dispersions of 510-TOP/TOPO in hexane with various amounts of excess caps. As shown in Fig. 6, the concave curvature near q=0 is progressively reduced with increasing excess cap. The suppression of the concave curvature at larger c_p reflects a recovery of the stabilizing repulsions. This recovery implies that a more effective screening of the van der Waals attractions is achieved with extra free caps. Such screening can be achieved if the caps pack around the surface, with their heads inward: "micellization" process. This provides a thicker, dense, liquidlike shell. Such a picture may be entropically unfavorable, but results from the affinity of the cap polar heads to the crystallite surface where most of the electronic activity takes place. It relies on a less favorable energy for the free caps in the solution, and is confirmed by the appearance of small micelles in the dispersion when the amount of excess caps becomes much larger (~ 10 times larger), since only a finite number of excess caps is necessary to fully passivate the nanocrystals. The micelles contribute to the scattering signal at large q, with the appearance of a finite intensity (small plateau) larger than the solvent background. The presence of micelles in the dispersions at higher excess free cap reflects an equilibrium between the crystallite surface and the dispersion. The two states that minimize the free energy of the polar heads on those caps are the particle surface and floating micelles.

2. Stable dispersions but attractive potential

This category includes nanocrystals capped with shorter alkyl chains, e.g., TBP/TBPO and PIC, dispersed in hexane and toluene, or butanol, respectively, and PYR capped crystallites dispersed in pyridine. In all cases, the capping groups have smaller lateral extension than TOP/TOPO. For the case of TBP/TBPO or PIC caps, the above treatment implies that the free energy of mixing ΔG_s^M is positive but still smaller than the van der Waals term, resulting in a shallow attractive potential, not strong enough to impart flocculation. For PYR capped particles in pyridine the situation is more subtle. Because the caps constitute an "innate" continuity of the surrounding solvent, the condition $\chi < 0.5$ is true and favors mixing. However, the caps are of molecular size, and their contribution to ΔG_s^M is small. This would result in an overall weakly attractive potential, but dispersions are stable. These attractions may result in association between the crystallites, e.g., the appearance of a small number of "dimers." The comparison of the experimental data to a mixture of two populations is a good first-order approximation because of the anticipated weak attractions between crystallites. The presence of a small fraction of "dimers," coexisting with the monomers, describes an equilibrium between the two "states" for the crystallites: single particles or "dimers." The crystallites move freely in the solution. Occasionally two particles come in contact; they stick together to form a "dimer" of finite life span.

3. Unstable, turbid dispersions

This category includes PYR capped crystallites dispersed in toluene and in hexane. These samples become turbid shortly after preparation. The precipitation is caused by an overall strongly attractive interaction potential. This results from the predominance of the van der Waals attractive potential over the mixing energy. The latter is small and possibly negative because of a smaller "stabilizing parameter" (due to low coverage, i.e., small ν_c and N), and a Flory parameter that does not favor mixing ($\chi > 0.5$). The pyridine shell is different from the surrounding solvent and has no lateral extension. It could neither alter the van der Waals attractions between cores, as is the case of TOP/TOPO, nor reduce them as in the case of PYR capped particles in pyridine.

VI. CONCLUSION

We presented a study of the properties of CdSe nanocrystal dispersions using x-ray scattering at small angles. The study provided accurate measurements of the size and size distribution, and a qualitative understanding of the interparticle interactions in the media. The primary factors that control the interactions, and define whether a dispersion is thermodynamically stable or not, are nature and spatial extension of the capping shell, degree of surface coverage, crystallite size, and solvent. Three types of solutions emerge from this investigation. (i) Sterically stabilized dispersions made essentially of nanocrystals capped with longer alkyl chains (octyl phosphine and octyl phoshine oxide), where favorable interactions between the caps and solvent dominate. This screens the van der Waals attractions between cores, and imposes a stability condition in these media. (ii) Dispersions of particles with a good surface coverage but small caps that have favorable interactions with the solvent. The short spatial extension of these caps provides only a modest screening of the van der Waals attractions. This results in dispersions governed by weak attractions, but not strong enough to induce flocculation. (iii) Last are nanocrystals with small caps that do not have favorable interactions with the solvent. The overall energy is attractive, and induces macroscopic precipitation.

The stability of the particles may be enhanced when a small amount of free alkyl caps is added to the medium. This is due to a natural tendency of the polar heads of the caps to approach the surface of the dot while hydrocarbon tails prefer to float in the solution. This cap excess increases the overall repulsion. However, one must be aware of the complexity of these systems. The above selective stability is not mainly caused by the affinity of the caps to the surrounding solvent. All the above caps and solvents are miscible in pairs, e.g., TOP and TOPO are soluble in all solvents. It is the affinity of the caps and core combined that defines whether a dispersion is stable or not.

ACKNOWLEDGMENTS

We thank M. Ken Kuno for stimulating discussions and for his assistance. M.G.B. thanks the David and Lucille Packard Foundation, the Sloan Foundation, and the W. M. Keck Foundation for funding. This research was funded in part by NSF Grant No. DMR-91-57491 and by the NSF-MRSEC program (Grant No. DMR-94-00034). Laboratoire de Physique de la Matière Condensée is a Unité de Recherche Associée au CNRS 792.

- *Present address: Naval Research Laboratory, Optical Sciences Division, Washington, DC 20375. Electronic address: hedimat@ccs.nrl.navy.mil
- [†]Present address: IBM T. J. Watson Research Center, Yorktown Heights, NY 10598.
- ¹M. L. Steigerwald, A. P. Alivisatos, J. M. Gibson, T. D. Harris, R. Kortan, A. J. Muller, A. M. Thayer, T. M. Duncan, D. C. Douglass, and L. E. Brus, J. Am. Chem. Soc. **110**, 3046 (1988).
- ²C. B. Murray, D. J. Norris, and M. G. Bawendi, J. Am. Chem. Soc. **115**, 8706 (1993).
- ³J. E. Bowen Katari, V. L. Colvin, and A. P. Alivisatos, J. Phys. Chem. **98**, 4109 (1994).
- ⁴M. A. Hines and P. Guyot-Sionnest, J. Phys. Chem. **100**, 468 (1996).
- ⁵Al. Efros and A. Efros, Fiz. Tekh. Poluprovodn. **16**, 1209 (1982) [Sov. Phys. Semicond. **16**, 772 (1982)].
- ⁶L. E. Brus, J. Chem. Phys. **80**, 4403 (1984).
- ⁷L. E. Brus, J. Phys. Chem. **90**, 2555 (1986).
- ⁸L. E. Brus, Appl. Phys. A: Solids Surf. **53**, 465 (1991).
- ⁹D. J. Norris, C. B. Murray, and M. G. Bawendi, Phys. Rev. Lett. **72**, 2612 (1994).

- ¹⁰D. J. Norris and M. G. Bawendi, Phys. Rev. B **53**, 16 338 (1996).
- ¹¹D. J. Norris, Ph.D. dissertation, Massachusetts Institute of Technology (1995).
- ¹²A. Fojtik, H. Weller, U. Koch, and Henglein, Ber. Bunsenges. Phys. Chem. 88, 977 (1984).
- ¹³C. R. Kagan, C. B. Murray, M. Nirmal, and M. G. Bawendi, Phys. Rev. Lett. **76**, 1517 (1996).
- ¹⁴C. R. Kagan, Ph.D. dissertation, Massachusetts Institute of Technology (1996).
- ¹⁵B. O. Dabbousi, M. G. Bawendi, O. Onitsuka, and M. F. Rubner, Appl. Phys. Lett. **66**, 1316 (1995).
- ¹⁶(a) M. C. Schlamp, X. Peng, and A. P. Alivisatos, J. Appl. Phys.
 82, 5837 (1997); (b) H. Mattoussi, L. H. Radzilowski, B. O. Dabbousi, E. L. Thomas, M. G. Bawendi, and M. F. Rubner, *ibid.* 83, 7965 (1998).
- ¹⁷J. Rodrigez-Viejo, K. J. Jensen, H. Mattoussi, J. Michel, B. O. Dabbousi, and M. G. Bawendi, Appl. Phys. Lett. **70**, 2132 (1997); and Mater. Res. Soc. Symp. Proc. **V452**, 365 (1997).
- ¹⁸B. O. Dabbousi, J. Rodrigez-Viejo, F. V. Mikulec, J. R. Heine, H. Mattoussi, R. Ober, K. J. Jensen, and M. G. Bawendi, J. Phys. Chem. **101**, 9463 (1997).

- ¹⁹(a) C. B. Murray, Ph.D. dissertation, Massachusetts Institute of Technology (1995); (b) J. P. Wilcoxon, R. L. Williamson, and R. J. Baughman, J. Chem. Phys. **98**, 9933 (1993); (c) P. J. Durston, R. E. Palmer, and J. P. Wilcoxon, Appl. Phys. Lett. **72**, 176 (1998), and references therein.
- ²⁰L. R. Becera, C. B. Murray, R. G. Griffin, and M. G. Bawendi, J. Chem. Phys. **100**, 3297 (1994).
- ²¹ M. K. Kuno, J. K. Lee, B. O. Dabbousi, F. V. Mukelec, and M. G. Bawendi, J. Chem. Phys. **106**, 9869 (1997).
- ²²H. Mattoussi, A. W. Cumming, C. B. Murray, M. G. Bawendi, and R. Ober, J. Chem. Phys. **105**, 9890 (1996).
- ²³A. Guinier and G. Fournet, *Small Angle Scattering of X-rays* (Wiley, New York, 1955).
- ²⁴A. Guinier and G. von Eller, in *Hanbuch de Physik*, edited by S. Flugge, Springer and Verlag, Heidelberg (1957).
- ²⁵ Small Angle X-ray Scattering, edited by O. Kratky and O. Glatter (Academic, London, 1982).
- ²⁶D. Espinat, Applications des Techniques de Diffusion de la Lumière, des Rayons X et des Neutrons à l'Etude des Systèmes Colloidaux (Editions Technip, Paris, 1990).
- ²⁷ Neutrons, X-ray and Light Scattering: Introduction to an Investigative Tool for Colloidal and Polymeric Systems, edited by P. Lindner and T. Zemb (North-Holland Delta Series, Amsterdam, 1991).
- ²⁸P. C. Hiemenz, *Principles of Colloid and Surface Chemistry*, 2nd ed. (Marcel Dekker, New York, 1971).
- ²⁹R. J. Hunter, *Foundations of Colloid Science* (Oxford University Science Publications, Oxford, 1987), Vol. 1, Chaps. 3 and 8.
- ³⁰J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Aca-

demic, London, 1976), Chaps. 2, 3, and 5.

- ³¹G. C. Berry, Adv. Polym. Sci. **114**, 233 (1994).
- ³²J. K. Percus and G. J. Yevick, Phys. Rev. **110**, 1 (1958); J. K. Percus, Phys. Rev. Lett. **8**, 462 (1962).
- ³³R. J. Baxter, Phys. Rev. **154**, 170 (1967); J. Chem. Phys. **49**, 2770 (1968).
- ³⁴J. Moonen, C. Pathmamanoharan, and A. Vrij, J. Colloid Interface Sci. 131, 349 (1989).
- ³⁵C. Regnault and J. C. Ravey, J. Chem. Phys. **91**, 1211 (1989).
- ³⁶S. Giasson, D. Espinat, T. Palermo, R. Ober, M. Pessah, and M. F. Morizur, J. Colloid Interface Sci. **153**, 355 (1992).
- ³⁷P. Roman, P. Hoornaert, D. Faure, C. Biver, F. Jacquet, and J. M. Martin, J. Colloid Interface Sci. **144**, 324 (1991).
- ³⁸(a) D. J. Deryck, J. Cebula, R. H. Ottewill, J. Ralston, and P. N. Pusey, J. Chem. Soc., Faraday Trans. 1 77, 2585 (1981); (b) C. Depege, D. Espinat, Y. Chauvin, H. Olivier, and R. Ober, J. Colloid Interface Sci. 158, 105 (1993).
- ³⁹H. Fujita, Polymer Solutions, Studies in Polymer Science (Elsevier, New York, 1990), Vol. 9.
- ⁴⁰P. J. Flory, J. Chem. Phys. **9**, 660 (1941).
- ⁴¹M. L. Huggings, J. Chem. Phys. 9, 400 (1941).
- ⁴²P. J. Flory, *Principles of Polymer Chemistry* (Cornell University Press, Ithaca, NY, 1953).
- ⁴³P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, NY, 1979).
- ⁴⁴N. Herron, J. C. Calabrese, W. E. Farnett, and Y. Wang, Science 253, 1426 (1993).
- ⁴⁵J. J. Shiang, A. Kadavanich, R. Grubs, and A. P. Alivisatos, J. Phys. Chem. **99**, 17 417 (1994).