Introduction

Nanoparticles have electronic, optical, and mechanical properties different from those of the bulk materials because of the large contribution of surface atoms.1−3 Hence, the precise size, shape, and surface chemistry of nanoparticles may be expected to have major effects on these properties.4−7

The unique and tunable properties of nanoparticles make them suitable for applications such as quantum dot displays, transistor, organic thin films, chemical and pressure sensors, and adhesion and friction modifiers, protective layers, and high surface area to volume ratio catalysts. Some of these applications require well-controlled shapes and concentration of surfactant-coated nanoparticle cores of ZnS nanospheres, nanorods, and nanowires on the normal (rather than shear) forces associated with confining these nanoparticles. At the same time, we have also tried to identify the optimum conditions for obtaining large areas of uniformly ordered nanoparticle films consisting of many nanoparticle layers. The nanoparticles studied were chosen due to the versatility of the synthesis, allowing for highly monodisperse nanostuctures of various well-controlled geometries composed of environmentally friendly ZnS as well as other materials.9,10 Furthermore, the surfactant coating on the surface of the nanoparticles controls particle−particle interactions and prevents their coalescence.

Experimental Methods

ZnS nanospheres, nanorods, and nanowires were synthesized using a method developed by Prof. Efrima at Ben Gurion University (BGU) as described by Pradhan et al.11 The nanorods and nanowires were coated with the surfactant octadecylamine (ODA, C18H33N) and the nanoparticles with hexadecylamine (HDA, C16H32N). All nanoparticles had ZnS core diameters of ~1 nm, an outer diameter of ~4 nm (including the ~1.5 nm thick surfactant layer), and lengths of 4.5, 8, and ~200 nm for the spheres, rods, and wires, respectively (Figure 1).

We used a surface forces apparatus (SFA)12−14 to measure the normal forces between two curved molecularly smooth surfaces of mica across (immersed in) dodecane containing various concentrations of the nanoparticles (the surfactant-coated nanoparticles could be dispersed in dodecane; in contrast, in many other heavier solvents they aggregate). The forces were measured using double-cantilever force measuring springs of stiffness ranging from 400 to 2300


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N/m (stiffer springs allow for higher forces to be measured but at a lower accuracy). The back surfaces of the mica substrates (~1–3 μm thick sheets) were coated with a ~50 nm thick semireflective layer of silver, required to obtain fringes of equal chromatic order (FECO), which were used to record—simultaneously and in situ—the surface separation, the surface shape and deformations and hence the uniformity of the trapped nanoparticle films, the “contact” area, and the mean refractive index of the films.13,15

The nanoparticles were dispersed in dodecane in a nitrogen-purged dry glovebox. Typical nanoparticle concentrations were between 0.01 and 4 mg/mL. Molecular sieves (8–12 mesh) were then added to the composite solutions to absorb any residual water. For the SFA experiments, a droplet of the appropriate dispersion was injected between two closely apposed mica surfaces and the SFA chamber was sealed in an atmosphere of dry nitrogen gas with a small Petri dish of P2O5 powder to ensure complete dryness during the experiments.

Dodecane was purchased from Sigma-Aldrich and was dried over molecular sieves (EM Science, type 4A, 8–12 mesh) prior to use. The muscovite mica was grade 1 muscovite mica, purchased from S & J Trading (Glen Oaks, NY). Phosphorus pentoxide (P2O5) was used as received from Fisher Scientific.

The forces in the absence of particles, i.e., in pure hydrocarbon liquids or liquids with surfactant only, have been extensively studied.12,16,17 In addition, we measured the forces between mica surfaces in a solution of hexadecylamine in dry dodecane and after the surfaces were exposed to humid air for some hours as a control experiment (described elsewhere).18

Results and Discussion

Effects of Nanoparticle Shape and Size. Figure 2 shows the measured forces between mica surfaces across dodecane containing ZnS–ODA nanorods. As can be seen, any attractive van der Waals forces between the surfaces or nanoparticles are negligible compared to the repulsive forces of compressing and aligning them between the two surfaces. An interesting aspect of the force profiles measured in these systems was that when the surfaces were brought together for the first time (“1st Run In”), there was a long-range exponential repulsion from 150 to about 50 nm, after which, on further compression, the surfaces

collapsed to a "hard-wall" repulsion at \( D \approx 13 \text{ nm} \), corresponding to 2–3 rod diameters together with one monolayer of surfactant on each mica surface. The regime between the “soft” exponential repulsion and the “stiff” hard-wall repulsion had an almost constant force (see solid circles in Figure 3), characteristic of a first-order phase transition (in this case, probably from a disordered state to an ordered state of aligned/oriented nanorods).

All successive force runs, whether on separation (“Out” curves) or approach (“In” curves), were reversible and did not exhibit any significant forces beyond the hard-wall separation at \( D \approx 13 \text{ nm} \).

These results suggest either that (i) a very long time (days) is needed for the system to return to its initial (equilibrium) state or (ii) the disorder → order transition is irreversible, i.e., that the compressed state is the equilibrium state (attained more quickly by the first compression). It is also clear that a monolayer of nanoparticles adheres quite strongly to the mica surface or to a monolayer of ODA strongly absorbed on the mica surface (there is excess surfactant in the nanoparticle solution), or else all the particles would have been squeezed out completely on the first approach with the surfaces coming into contact at \( D = 0 \). The fact that the material piled up on the first layer was easily squeezed out suggests that nanoparticle–nanoparticle adhesion is relatively weak (compared to the nanoparticle–substrate adhesion).

Figure 3 shows the forces at the same mass concentration as in Figure 2 (\( c = 0.05 \text{ mg/mL} \)) for the spheres, rods, and wires. These curves are the “reversible” curves, i.e., after the first compression. Again no significant adhesion was measured at any separation. The smallest particles (the spheres) exhibited the smallest repulsion, and the largest particles (the wires) exhibited the largest. Again, the forces were roughly exponential, and again some interesting additional features, suggestive of structural transitions or rearrangements, could be observed, such as the near-constant forces from 20 to 30 nm for the nanorods and from 50 to 60 nm for the nanowires and a constant slope force regime from 30 to 35 nm for the nanorods. The hard-wall distances increased with the size of the particles: ~4–5 nm for spheres, ~13 nm for rods, and ~14 nm for wires.

The bulk concentration of \( c = 0.05 \text{ mg/mL} \) corresponded to volume fractions of \( 5 \times 10^{-5} \). However, the volume fraction in the confined solution increased as the surface separation decreased. The increased nanoparticle densities in the films could be determined from the measured refractive index of the films. These measurements showed that the volume fractions or “packing densities” of the nanoparticles gradually increased as \( D \) decreased, until they reached a value close to the close-packed density, typically ~0.72 ± 0.05 (~72 ± 5%) at separations of \( D \approx 3 \text{ nm} \).

**Effects of Bulk Nanoparticle Concentration.** Figure 4 shows the reversible force profiles for the various nanoparticles in dodecane at bulk concentrations of 2 mg/mL (40 times higher than the concentrations used in Figures 2 and 3), which corresponds to bulk volume fractions of \( 1.86 \times 10^{-3}, 2.06 \times 10^{-3}, \) and \( 2.15 \times 10^{-3} \) for nanospheres, nanorods, and nanowires, respectively. The magnitude and range of the forces were again in the order spheres < rods < wires. The forces were again always repulsive, and the repulsion was roughly exponential, but the rods and wires now display more sigmoidal force profiles when measured over 4 decades (with no discernible hysteresis). At short distances, the forces have roughly the same exponential decay length.

Nanoparticles in progressively more concentrated solutions tend to aggregate, cluster, and precipitate out of the bulk solution. For ZnS–ODA nanorods in dodecane this occurs at \( c \approx 4 \text{ mg/mL} \). The forces in 4 mg/mL nanorod solutions, where the bulk dispersion was stable for a limited time, are shown in Figure 5. The forces were still repulsive and roughly exponential. One can also notice small features such as constant force regimes at around 130 and 170 nm.

Figure 6 shows the effect on the force profiles of a 200-fold change in the bulk concentration of ZnS–HDA nanospheres in dodecane. The concentration ranged from 0.01 to 2 mg/mL, corresponding to bulk volume fractions ranging from \( 4.65 \times 10^{-5} \) to \( 1.86 \times 10^{-3} \). The following additional observations can be made: (i) the more concentrated the nanospheres solution, the larger the normal forces, (ii) the hard-wall distance was larger for more concentrated solutions, and (iii) kinks and discontinuities were more evident for more concentrated solutions. As can be seen from Figures 2–6, the particle layers interact considerably when the surfaces are closer than a couple of hundred nanometers. This is presumably due to particle entanglement and/or interdigitation of the surfactant groups. As the nanoparticles are increasingly confined, their volume fraction increases so that the “steric repulsion” increases. Analogously, the more concentrated solutions have a larger volume fraction right from the...
start. This can explain the increasing forces with decreasing separation or increasing bulk concentration.

Analysis of the Fine Features (Kinks, Horizontal Regions) of the Force Curves. As already mentioned, the near-constant force regions in Figures 3 and 5 are suggestive of phase transitions in the films, of which there could be many. This would be analogous to (or due to) the oscillatory forces that arise during the confinement of hard or symmetrical liquid molecules, liquid crystals, and small colloidal clusters, e.g., nanoparticles and concentrated micelles, forcing them to order into quasi-discrete layers. Oscillatory forces do not require any attractive liquid—liquid or liquid-wall interaction, only two hard walls confining molecules or particles whose shape is not too irregular and that are free to exchange with the molecules in the bulk liquid reservoir. Such forces have a mainly entropic origin, which includes excluded volume effects that determine how the molecular size and shape enter into the picture. The main differences between the oscillatory forces of simple liquids and the nanoparticles we have used here are (i) the oscillatory forces for nanoparticles are much longer ranged than those for simple liquids, (ii) the characteristic times for the transitions and relaxations appear to be very much longer, and thus, we observed much longer times for the various instabilities, such as the “spontaneous” jumps from one separation to another that occur when forces that have positive slopes in them are measured, than

Figure 4. Reversible force profiles between surfaces during approach in dry conditions: (a) linear scale; (b) logarithmic scale. Bulk ZnS nanoparticle concentration $c \approx 2$ mg/mL for each system.

Figure 5. Forces between mica surfaces across superconcentrated nanorod dispersions in dry conditions: (a) linear scale; (b) logarithmic scale. ZnS nanorod concentration $c \approx 4$ mg/mL (metastable solution).

Figure 6. Effect of concentration on the normal force profiles for ZnS–HDA nanospheres in dodecane. Bulk concentrations 0.01–2 mg/mL. Inset: same data plotted on a log scale.
for simple liquids, and (iii) for nanoparticles the jump distances or discontinuities often involve multiple layers, rather than the single layers typically seen with simple liquids.

This suggests that these nanoparticles may aggregate/cluster into multiparticle units ("polycrystals" or "supercrystals") when they order into a nanostructured film or material. Figure 7a,b shows AFM images of the ZnS nanowires adsorbed to mica after drying (sample taken from a real experiment after it has ended). We see well-structured aggregates as well as superaggregates or aggregates of aggregates\textsuperscript{25} (Figure 7b)—the former likely signifying the hard-wall layer and the latter the longer ranged monotonic repulsion. Similar grains or polycrystals consisting of different numbers of particles are observed for other systems such as polystyrene rods: Figure 7c shows an assembly of more macroscopic rodlike particles of polystyrene that display a mix of short-range ordering (aggregates) that adhere to other aggregates.

We point out, however, that even if we sometimes observed fine features in the force profiles that provide insights into nanoparticle rearrangements, when considered over many orders of magnitude, the forces are essentially (in a first approximation) exponential, which also has no current theoretical explanation.

**Effects of Small Amounts of Water (Increased Water Activity or Humidity).** To better understand the effects of the presence of water on surfactant-coated nanoparticle interactions, we first investigated the effects of water on the dissolved surfactant alone. Forces between mica surfaces across dodecane containing only hexadecylamine were measured in the absence and presence of water. As shown in Figure 8, on approach in dry surfactant solution, the surfaces experience a weak repulsion and then a steep repulsion from $D = 10$ nm to the hard wall at $D = 6$ nm. Introduction of water into the dodecane via the vapor (by increasing the relative humidity to $94\%$ - $97\%$) changed the force profile both quantitatively and qualitatively: (i) the distance at which the repulsion was first felt increased, (ii) the repulsion varied almost linearly with $D$ from 30 to 20 nm, and (iii) the hard-wall distance increased to $D = 16$ nm. Similar force profiles were observed for other surfactant—oil—water systems,\textsuperscript{26,27} Chen et al.\textsuperscript{26,27} proposed that water penetrates into the hydrophilic headgroup—substrate region of physisorbed monolayers, which causes swelling. This swelling is responsible for the increased range of the repulsive force and also for the larger hard wall.

Figure 8 shows the measured forces across dodecane containing ZnS—ODA nanorods, again in the absence and presence of water.

\textsuperscript{25} Such supercrystalline aggregates have been confirmed using TEM (see Figure 1b,c), XRD, and GIXD and will be reported elsewhere.


It is also important to mention that each run was carried out at different contact positions of the two surfaces to eliminate the possible effect of history and multiple compression cycles. This is readily achieved in the SFA experiments by laterally moving one of the surfaces, thanks to cross-cylinder geometry. In dry solution, little or no force is felt on approach until the surfaces are $40 \text{ nm}$ apart, and the surfaces reach a hard wall at $D = 12 - 15 \text{ nm}$, as before (cf. Figure 3). In wet dodecane, both the repulsion and hard-wall thickness increase with increasing time of exposure to humid vapor.

Figure 10 is very similar to Figure 9 except that the contact position was kept the same instead of being changed. Thus, it shows the combination of two counteracting effects of previous history and time: the time of exposure to wet solution (between compression–decompression cycles), which increases the repulsion due to swelling, and the number of previous cycles, which decreases the repulsion due to the compression of the adsorbed layers.

When the surfactant layer is lifted from the ZnS cores by a layer of water, aggregation via capillary forces can now occur as previously observed and described in similar colloidal systems, or even via attractive van der waals forces can occur. These plastically deformable aggregates occur in solution as well as on the surfaces (Figure 9). Their thickness on the surfaces increases with time of exposure to humid vapor, while each compression further orders the nanorods in the surface film. Thus, there is a complex interrelationship among the effects of time, number of force cycles, and nanoparticle ordering in the film as well as the maximum compressive pressure (minimum film thickness) attained during each run. Thus, we note two important differences in the force profiles in the dry and wet systems: in the wet systems the forces are almost linear rather than exponential, and also not fully reversible.

After a very long exposure to humid air ($t > 20 \text{ h}$), the system develops a strong long-range attraction. That is because when the amount of water increases to saturation, a continuous water meniscus bridges the two surfaces, and the Laplace pressure exceeds the jamming repulsion: the surfaces jump into contact. In other words, the capillary force between the surfaces now dominates the interaction between them.

In light of these results, we propose the following explanation for the effects of water on physisorbed surfactant-coated nanoparticle dispersions in organic (hydrophobic) solvents (Figure 11): Under dry conditions, the surfactant binds to the core surface and therefore efficiently shields it from the solution and other particles and surfaces (Figure 11a). In wet conditions (depending on the amount of water in the solvent), a thin water film builds up between the surfactant head groups and ZnS core surfaces, causing their aggregation into semirigid flocs and increased adhesion to any hydrophilic, such as mica, surfaces. In panel b (iii), depending on the amount of water, the capillary bridges can be between the nanoparticles or between the two (macroscopic) surfaces.


![Figure 9](image)

**Figure 9.** Forces between mica surfaces in dodecane containing 0.05 mg/mL ZnS–ODA nanorods during approach after different exposure times to humid vapor ($n =$ number of layers).

![Figure 10](image)

**Figure 10.** Forces between surfaces during successive approaches and separations (“In”−“Out” cycles or runs) in wet dodecane. In each approach run the surfaces were brought to the hard-wall distance and then separated, and the cycle was repeated after exposure times to humid vapor of ~10, 15, 30, and 120 min (solution conditions as in Figure 9).

It is also important to mention that each run was carried out at different contact positions of the two surfaces to eliminate the possible effect of history and multiple compression cycles. This is readily achieved in the SFA experiments by laterally moving one of the surfaces, thanks to cross-cylinder geometry. In dry solution, little or no force is felt on approach until the surfaces are ~40 nm apart, and the surfaces reach a hard wall at $D = 12 - 15 \text{ nm}$, as before (cf. Figure 3). In wet dodecane, both the repulsion and hard-wall thickness increase with increasing time of exposure to humid vapor.

Figure 10 is very similar to Figure 9 except that the contact position was kept the same instead of being changed. Thus, it shows the combination of two counteracting effects of previous history and time: the time of exposure to wet solution (between compression–decompression cycles), which increases the repulsion due to swelling, and the number of previous cycles, which decreases the repulsion due to the compression of the adsorbed layers.


with those adsorbed on any nearby surfaces. This causes the increase in the surface separations at which the repulsion is felt as observed in Figures 9 and 10.

Comparison with Similar Systems. Gourdon et al.\textsuperscript{30} used an X-ray surface force apparatus to investigate the effects of normal load and shear on the ordering of 10 nm × 30 nm surfactant-coated BaCrO\textsubscript{4} nanorods in isooctane. They also observed roughly exponential forces as a function of surface separation and alignment of the rods with successive compressions and shear.

Golan et al.\textsuperscript{31} measured the forces between thin films of nested inorganic fullerene (IF) nanospheres and nanotubes of MX\textsubscript{2} (where M = W or Mo, and X = S or Se) in tetradecane and observed long-range linear repulsive forces. The diameters of the IFs ranged from 20 to 30 nm. It is important to note that these nanoparticles were not coated with any surfactant and that the bulk dispersions were unstable due to the strong van der Waals attraction between the “unprotected” particles. It is noteworthy that, both in this case and in the case where water was present in dodecane containing ZnS–ODA nanoparticles, the forces between the nanoparticles were attractive (adhesive), resulting in a linear $F(D)$ profile (straight line repulsion) between the confining surfaces, rather than an exponential one.

Kudrolli et al.\textsuperscript{32} used millimeter-sized hard spherical particles to study granular hydrodynamics. They observe strong aggregation or clustering of particles as their density is increased. They also showed that probability distributions of the local number density decrease roughly exponentially with decreasing surface separation when one of the surfaces is vibrated (compressed) at a certain frequency. It is noteworthy that even if there are 6 orders of magnitude differences in particle sizes, similar trends are observed for nanoparticles (even the origins of the forces could be totally different).

Comparing the Forces and Energies between Particles and Flat (Planar) Surfaces. The Derjaguin approximation

$$F(D) = 2\pi R[E(D)]$$

(1)

allows us to relate the force-distance curve $F(D)$ between two curved surfaces of radius $R$ to the interaction free energy $E(D)$ between two planar surfaces at the same separation $D$. In other words, the (measured) force between our curved surfaces is proportional to the interaction energy between two flat plates.

The pressure between two surfaces is simply calculated as follows:

$$P(D) = -d[E(D)]/dD = -[d[F(D)]/dD]/2\pi R$$

(2)

For instance, the linear force vs distance region between two curved surfaces, as seen in Figures 9 and 10, implies a constant pressure vs distance (or volume) between two planar surfaces. Since a constant pressure between two plates corresponds to a linear energy between the plates (i.e., an energy function of constant slope, not constant magnitude), a linear force measured between our curved surfaces therefore corresponds to a linear energy between two plates and hence to a constant pressure regime, which is the sign of a first-order phase transition. This transition is more likely to be an athermal, purely particle-geometry-dependent, order–disorder transition of the Kirkwood–Alder type rather than a thermal origin. Given the asymmetric shapes and range of sizes of our particles, a number of such structural transitions could occur at different volume fractions (confinement) and pressures. Importantly, neither Kirkwood–Alder transitions nor those due to oscillatory forces require any attractive forces between the molecules or particles. Attractive forces and temperatures probably do play a role in the transitions involving the smaller, especially spherical, nanoparticles we have studied. The quantitative importance of these effects requires further studies.

The measured force $F(D)$ between two rigid, i.e., undeformable, crossed cylinders each of radius $R$ can be related to the energy per unit area $E(D)$ between two flat surfaces at the same separation $D$ by the Derjaguin approximation, eq 1.\textsuperscript{23} Typically, $R \approx 2$ cm for the experiments carried out here. The adhesive pressure $P(D)$ between these surfaces can be calculated from eq 2. At large loads, the glue supporting the mica substrates starts to deform noticeably, at which point the Derjaguin approximation is no longer valid. When this occurs, the surfaces locally flatten, and the diameter $2r$ of the flattened region can be measured from the shapes of the FECO fringes. Under these conditions, since the surface separation $D$ and applied load or force $F(D)$ are also measured, the pressure between surfaces can be obtained directly from

$$P(D) = F(D)/\text{area} = F(D)/\pi r^2$$

(3)

Figure 12 shows the pressures between the two surfaces of Figures 3 and 6 in the low-load/low-pressure regime using only


surfaces on the basis of the data of Figure 5 on logarithmic scales. There are also some similar features of the particles. However, long-range tails appear to be controlled and therefore the ordering is mainly governed by the diameters decay length, suggesting that the high pressure at small separations types of nanoparticles approximately have the same exponential small separation (Figure 12b). It is also very interesting that all the pressure is roughly exponential with respect to distance at high concentration as expected from force profiles. In addition, eq 2 at various concentrations. One can note that (i) the pressures have spikes at certain locations for all types of nanoparticles, suggesting instabilities (discontinuities) in the layered structure and/or first-order phase transitions, (ii) the spikes appear at larger separations for the larger particles, (iii) the spikes do not show any definite periodicity, and (iv) there is a phase transition corresponding to disorder—order transition in nanoparticle systems where Gibbs free energies and pressures of the two phases are equal. However, since thermal effects are important and the surfaces are brought together with a finite velocity, there are fluctuations in the phase diagram.

Figure 13 shows the pressures of Figure 5 at high concentration. One can immediately notice that the pressures are much larger at high concentration as expected from force profiles. In addition, the pressure is roughly exponential with respect to distance at small separation (Figure 12b). It is also very interesting that all types of nanoparticles approximately have the same exponential decay length, suggesting that the high pressure at small separations (and therefore the ordering) is mainly governed by the diameters of the particles. However, long-range tails appear to be controlled by the size of the particles. There are also some similar features between high- and low-concentration pressure profiles such as “spikes” (Figures 12 and 13). However, since the forces are much larger and longer ranged at higher concentration, the relative magnitudes of the spikes with respect to forces due to other contributions are smaller. It appears that there is no characteristic distance for the jumps or instabilities.

Origin of the Forces. Some of the likely sources of the repulsive (and sometimes attractive) forces have already been discussed above. Possible forces can be listed as follows: electrostatic double-layer forces and ionic bonds, entropic thermal fluctuation forces, van der Waals forces, structural forces, forces associated with elastic (reversible) and plastic (irreversible) deformations, and friction forces. However, as mentioned before, some of these contributions are small. For example, the entropic thermal fluctuations could only be responsible for the fine details in the force profile and can play a role at dilute concentrations and for small-sized particles.

Under dry conditions, ionic bonds may be responsible for the adhesion of the surfactant to the ZnS surface, especially if there is some charge transfer (of a proton) occurring from the ZnS atoms to the amine head group. Under wet conditions, a double-layer force is expected to arise across the swollen water film between the ZnS surfaces and amine head groups. However, repulsive structural, steric hydration, and thermal undulation forces are also expected to arise across these thin water films.

We observed roughly exponential repulsions for dry nanoparticle systems and roughly linear repulsions for (partially) wet systems. In wet conditions, the surfactant monolayers are no longer strongly attached to the nanoparticle cores and can move freely, encapsulating both single nanoparticles and aggregates (Figure 10). Golan et al. also obtained a linear force profile for bare (adhering) nanoparticles. These suggest that the surfactant layers, which produce little or no force between the nanoparticles in the hydrocarbon solvent (except for a very weak van der Waals force and a quasi-hard-core steric repulsion), are responsible for the exponential repulsions. More generally, one may say that noninteracting nanoparticles oppose being confined via an exponentially repulsive pressure, while adhering particles do this via a linear repulsion.

Regarding irreversible linear repulsive behavior, we only observed this type of forces in wet solutions, when the surfactant layers are mobile and when the nanoparticles aggregate to form nanoclusters. When we compress such structures, especially at very high loads, they deform irreversibly, i.e. plastically. If we consider the theory of a plastically deforming spherical body on a flat substrate (Figure 14) (unlike an elastic sphere as in the JKR theory), the relationship holds, so that

\[ H = \frac{F}{\pi r^2} \approx \frac{F}{2\pi RD} \]

which results in a linear force profile, as observed in Figures 8 and 9.

Regarding the effect of particle geometry on the forces, when the force profiles of the different nanoparticles are compared, they show much larger differences at large separations than at small separations, where they all collapse to roughly the same value within \(\sim 10\) nm (corresponding to a few particle diameters)

\[ F = 2\pi RDH, \quad \text{i.e.,} \quad F \propto D \]


Figure 4. The long-range onset distances of the repulsive forces were in the following order: nanowires > nanorods > nanospheres, indicating that the larger dimension (the length) of the particles determines the long-range force, while the smaller dimension (the width or rod/wire diameter) determines the short-range force. We would also mention that with these systems one needs to wait for much longer times (days) to obtain the thermodynamic state and interaction potential. Figure 14 illustrates the likely structural changes occurring during the confinements, consistent with our force measurements.

Conclusions

We have studied the effects of the molecular size, shape, and concentration of various types of surfactant-coated nanoparticles on the normal forces across nanometer thick nanoparticle films using the surface force apparatus. Forces were exponentially repulsive when the surfactant layers were strongly attached to the nanoparticles and were roughly linear when there was adhesion between the nanoparticle cores, i.e., when surfactant layers detached from the nanoparticles. In both cases, the range and magnitude of the forces changed with particle size and with solution concentration. Even when the forces were mainly exponential as in the dry system, fine details such as local constant force or linear force regions were observed in the force profiles. Local constant force regimes were also seen in the linear force profiles. The constant force (plateau) regions suggest structural reorganization of nanoparticle layers, and the linear force regions signify first-order phase transitions such as an order–disorder transition in the dry systems, and/or irreversible plastic reordering in the wet systems. Overall, our results suggest that, in these systems, the sizes and strengths of the forces between the nanoparticles make the system fall into a regime where equilibrium thermodynamics may no longer apply at the time scales of the measurements. Parts of the systems appear to be in (local) equilibrium, while others, such as jammed regions, are not.

The results, while complex, appear to be qualitatively explainable and consistent with current theories of interparticle forces in liquids. However, more involved numerical simulations or theories are needed to explain the quantitative details of the force profiles. They are also likely to be of relevance to other nanocomposite material systems and processes. These effects can have important implications for the processing of nanoparticles into thin uniform films and into potentially useful nanostructured materials with desirable properties.

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