Computer simulations and thermodynamics of anisotropic nanoparticles at fluid interfaces

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Abstract. We investigate the applicability of thermodynamic models to investigate the physical behavior of nanoscale objects at liquid-liquid interfaces. The applicability of such models to these small scales is not obvious, since they ignore the molecular nature of the solvent, finite width of the interface, or fluctuations. We focus our study on anisotropic nanoparticles that can interact with an external field through an embedded dipole moment. Using Monte Carlo simulations we show that thermodynamic models defined in terms of a few material properties very accurately describe the behavior of nanoparticles in a wide range of conditions; field strength, nanoparticle-fluid interactions and nanoparticle size and anisotropy. Our results show that thermodynamics offers a powerful approach to investigate the physical behavior of nanoscale objects. **Submitted to the Proceedings of the StatPhys 23 conference**

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1 Introduction

Colloidal nanoparticles of sizes 3-100 nm, can adsorb very strongly at fluid (liquid-vapor or liquid-liquid) interfaces. An estimate of the adsorption energy in terms of simple thermodynamic models suggest energies between 10 and $10^3 k_B T$. This high energy provides a route to make well defined two dimensional arrays and crystals. Such struc-

tures are of interest in condensed matter physics, as experimental models to investigate two dimensional phase transitions [1–3]. Fluid interfaces can also be used as a substrate for the self assembly of nanoparticles into materials with specific properties; mechanical, optical, or magnetic [4]. Unlike solid surfaces fluid interfaces are defect free. This fact can be used to minimize the transfer of undesirable epitaxy effects from the substrate to the material.

Recent experiments have shown that nanoparticles adsorbed at interfaces can behave very different as compared with particles in bulk. Nanoparticles form complex structures, whose origin is not well understood. The interactions are expected to be very different from the interactions in bulk. To start with the nanoparticles move on a fluctuating surface. It has been shown that this can lead to weak Casimir like attractive interaction [6,7]. In the case of nanoparticles with complex shapes or chemically heterogeneous, capillary interactions may arise from the interfacial deformation around the nanoparticles. Also, the break of symmetry at the interface, which separates media with different dielectric permittivities, can have important effects on the van der Waals and Coulombic interactions. These situations have been discussed recently by us in a extensive review [8].

The experimental characterization of the contact angle and orientation of nanoparticles at interfaces offers a number of challenges. Optical methods that are normally used at the microscale are not useful at the nanoscale. In fact, there are not experimental techniques capable of providing reliable quantitative information on the surface tensions and line tensions of small nanoparticles, or alternatively geometric realizations of these, i.e., contact angles. Nonetheless, it has been shown recently that the use of thermodynamic theories and computer simulations can provide important insights into the physical behavior of these systems. In particular computer simulation techniques offers an alternative to test the applicability of thermodynamic theories to nanoparticle systems, i.e., small

systems, which represents a significant scientific challenge [5].

The thermodynamic theories take advantage of the small size of the system (nm), much smaller than the interfacial capillary length (mm). Hence, unlike larger colloidal systems approaching the macroscopic scale, the theoretical treatment of nanoparticles can be simplified, because gravitational effects can be ignored. It is important to note that a full statistical mechanics treatment of nanoparticles at interfaces is a current challenge in condensed matter physics theory.

The interplay between nanoparticle geometry and interfacial forces in non-spherical nanoparticles results in a very rich physical behavior. The adsorption energies are strongly dependent on the nanoparticle shape; disc like particles showing the largest energies. Moreover the line tension can strongly modify the stability of anisotropic nanoparticles [9]. Hence positive line tensions (≈ 10 pN) can destabilize elongated objects (nanotubes, fibers). This notion suggests a route to indirectly assess the order of magnitude and sign of the line tension in experimental studies.

The interaction of anisotropic nanoparticles with external fields (electric, magnetic) also exhibits a complex behavior. Thermodynamic treatments predict a discontinuous jump in the orientation at a specific field strength. In this paper we extent our previous work on anisotropic nanoparticles at interfaces in the presence of external fields. We test the applicability of the thermodynamic models to these small scales. We address specifically two variables, nanoparticle size and nanoparticle anisotropy.s). This no-

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2 Thermodynamic model

In this paper we concentrate on the physical behavior of one nanoparticle adsorbed at a fluid interface. This situation is representative of nanoparticles at very low coverage, and therefore we ignore as a first approximation nanoparticle-nanoparticle interactions. Thermodynamic models describe the free energy of nanoparticles at interfaces in terms of a few parameters; surface tensions, geometrical quantities (surface areas, three phase line length) and line tensions. The applicability of such models to small systems is not obvious a first sight, since they neglect the molecular nature of the solvent, or the interface width, which can be of the order of the nanoparticle size. Nonetheless, we have shown that the thermodynamic approach very accurately describes the behavior of small nanoparticles at liquid-vapor and liquid-liquid interfaces in a wide range of conditions [11–13].

Fig. 1. Sketch of spherical and an ellipsoidal nanoparticles at a fluid-fluid interface. 1 and 2 represent the fluid phases, and the symbols different quantities defined in the text.

The free energy of the nanoparticles at the interface can be written as,

$$F_{int} = (\gamma_{p2} - \gamma_{p1})A_{p2} - \gamma_{12}A_{st} + \tau L \quad (1)$$

where γ_{p2} , γ_{p1} are the particle fluid surface tensions, A_{p2} is the area of the nanoparticle-fluid interface, A_{st} is the fluid interfacial area removed by the nanoparticle (c.f. Figure 1), γ_{12} is the surface tension of the fluid-fluid interface and τ is the line tension of the three phase line. The free energy in equation 1 is written with reference to the free energy of the particle fully immersed in one of the phases [8].

Anisotropic nanoparticles can be represented as ellipsoidal objects. The nanoparticle geometry is defined in this instance by the aspect ratio, α and the eccentricity, ϵ ,

$$\alpha = \frac{z_m}{r_m} \quad (2)$$

$$\epsilon = \sqrt{1 - \alpha^{-2}} \quad (3)$$

where z_m and r_m represent the major and minor axis of the ellipsoid. In this paper we consider elongated nanoparticles (fibers, nanotubes) and therefore $\alpha \geq 1$. The total area of the nanoparticle, $A_p = A_{p1} + A_{p2} = 4\pi r_m^2 G(\alpha)$

can be defined in terms of the geometrical aspect ratio, $G(\alpha)$ [9],

$$G(\alpha) = \frac{1}{2} + \frac{1}{2} \frac{\alpha}{\epsilon} \arcsin \epsilon \quad (4)$$

With these definitions it is possible to derive explicit expressions for the free energy of anisotropic nanoparticles in different orientations (see references [9,10]).

In order to account for the interaction of the nanoparticle with the external field an extra term needs to be added to the free energy. We consider a model where the nanoparticle has an embedded electrostatic or magnetic permanent dipole. The interaction of this dipole with an external field will result in a torque that changes the nanoparticle orientation. Following our previous work we assume a free energy contribution of the form, $F_{ext} = -B \cos \phi$, where $B = |\mu| |\mathbf{H}|$ is the field dipole strength, and μ and $\mathbf{H}$, the dipole and field respectively. The free energy for the particle at the interface in the presence of an external field is given by,

$$F_{int} = -\gamma_{12} A_{st} + (\gamma_{p2} - \gamma_{p1}) A_{p2} + \tau L - B \cos \phi \quad (5)$$

where ϕ denotes the nanoparticle orientation (see Figure 1).

In the following we concentrate the interplay between particle shape and external field. With this purpose we consider a situation where the nanoparticle has the same affinity for both phases, $\gamma_{p2} = \gamma_{p1}$ and we ignore the effects of the line tension. This is a reasonable approximation *if* we consider high surface tension interfaces (≥ 10 mN/m) [13]. In order to calculate A_{st} we need to take into account the shape of the three phase line. Non vertical orientations

results in a three phase line that is undulated (according to Laplace equation). To obtain an analytical expression we assume a flat three phase line. The accuracy of this approximation will be tested below against exact Monte Carlo computations. The final expression for the free energy is given by [10],

$$F_{int}(\theta) = \frac{F_{int}(\theta)}{A_p \gamma_{12}} = -\frac{\alpha}{4G(\alpha)} \sqrt{\frac{1}{\cos(\theta)^2 + \alpha^2 \sin(\theta)^2}} - \frac{B \cos(\pi/2 - \theta)}{A_p \gamma_{12}} \quad (6)$$

3 Monte Carlo simulations of anisotropic nanoparticles at interfaces

Computer simulations offer an independent approach to test the accuracy of thermodynamic theories in describing complex interfacial problems. Recently we introduced a method to simulate anisotropic nanoparticles at fluid-fluid interfaces [10]. We considered a nanoparticle adsorbed at a fluid-fluid interface, where the two phases, ‘1’ and ‘2’ are immiscible one each other. The liquid-liquid interactions were modeled through the truncated and shifted Lennard-Jones potential,

$$u_{ij}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \xi_{ij} \left(\frac{\sigma}{r} \right)^6 \right] - u_{cut} \quad (7)$$

where ϵ and σ are the interaction strength and effective diameter of the particles respectively, u_{cut} is the energy at the potential cutoff, $r_{cut} = 2.5\sigma$, and ξ_{ij} is a parameter that tunes the attractive interaction. In this work $\xi_{ii} = 1$ for interactions between particles of the same species, and $\xi_{ij} = 0$ for unlike particles. All the simulations were performed using Monte Carlo simulations in the canonical

ensemble. The displacement of the particles was adjusted to provide an acceptance rate of about 50 %. The simulation involved over $N = 3 \times 10^4$ particles arranged in a prismatic box, $L_y = L_z = 29.4 \sigma$ and $L_x = 2L_y$. We investigated thermodynamic states away from the coexistence conditions of the isolated liquids. The temperature was set to $T^* = \beta^{-1}/\epsilon = k_B T/\epsilon = 1.0$ which results in a pressure, $P^* = P\sigma^3/\epsilon = 0.44$. Under these conditions the liquid densities are $\rho^* = 0.69$, and the interfacial tension is, $\gamma^* \approx 1$ (≈ 15 mN/m considering parameters for Argon).

The nanoparticle was modeled as an ellipsoid that interacts with the fluid through the Gay-Berne potential [14, 15]

$$u_{pf}(\mathbf{v}, \mathbf{r}) = 4\epsilon_{pf} \left[\left(\frac{\sigma}{r - \sigma_{pf}(\mathbf{v}, \mathbf{r}) + \sigma} \right)^{12} - \left(\frac{\sigma}{r - \sigma_{pf}(\mathbf{v}, \mathbf{r}) + \sigma} \right)^6 \right] - u_{cut} \quad (8)$$

where $\mathbf{v}$ is a vector defining the direction of the major axis of the nanoparticle, and $\mathbf{r}$ is the vector between the center of the nanoparticle and a liquid particle. ϵ_{pf} and $\sigma_{pf}(\mathbf{v}, \mathbf{r})$ represent the interaction strength and the effective diameter respectively, and u_{cut} is the nanoparticle-liquid potential energy at the cutoff distance, 2.5σ . The effective diameter, $\sigma_{pf}(\mathbf{v}, \mathbf{r})$ is given by,

$$\sigma_{pf}(\mathbf{v}, \mathbf{r}) = \sigma_{\perp} \left[1 - \chi \left(\frac{\mathbf{r} \cdot \mathbf{v}}{|\mathbf{r}| |\mathbf{v}|} \right)^2 \right]^{-1/2} \quad (9)$$

where $\chi = (\sigma_{\parallel}^2 - \sigma_{\perp}^2)/\sigma_{\parallel}^2$, $\sigma_{\parallel}^2$ and $\sigma_{\perp}^2$ being the major and minor axes respectively.

Following the thermodynamic model, the nanoparticle-fluid surface tension was the same for both fluids. There-

fore we set the same nanoparticle-liquid interaction, $\epsilon_{p1} = \epsilon_{p2} = 1.5\epsilon$. Other interaction strengths were also considered to address the effect of the solvent-nanoparticle interactions. In addition we investigated different aspect ratios as well as different nanoparticle sizes.

The interaction of the nanoparticle with the external field is given by,

$$U_{ext}(\phi) = -B \cos \phi, \quad (10)$$

where again ϕ is the angle between the dipole vector (i.e the major axis of the ellipsoid) and the external field, which is normal to the liquid-liquid interface, and B is the strength of the external field.

A typical simulation involved $3\text{-}5 \times 10^5$ steps. Each step consisted of N attempted displacements, as well as one attempt of changing the nanoparticle orientation.

4 Testing thermodynamic models in nanoscale systems

The thermodynamic model allows us to investigate the response of the nanoparticle to the external field. This model predicts a monotonic variation of the nanoparticle orientation with the external field. Interestingly we found in an earlier work that the model features a discontinuous jump at a characteristic external field strength. The magnitude of this ‘critical’ field is determined by the interfacial tensions and the nanoparticle geometry. Figure 2 shows an example of the variation of the nanoparticle orientation with the external field [10]. The simulation results

Fig. 2. (Left) Variation of nanoparticle orientation with the external field for nanoparticles with aspect ratio, $\xi = 1.66$ and size $8\sigma \times 4.8\sigma$ (black points) and $5\sigma \times 3\sigma$ (white symbols). (Right) Free energy of the nanoparticle as a function of orientation for field strength $B/(A_p\gamma_{12}) = 0.169$.

are well described by the thermodynamic theory, which ignores the interfacial width, interface fluctuations as well as other effects such as the line tension. Our simulations showed that the nanoparticle had a preference to adopt two distinct orientations at a specific field strength, suggesting the possibility of an orientational transition, as predicted by the theory. In small systems such as these ones, one would expect nonetheless that the transition will be smoothed by the fluctuations. This would be reflected in the height of the energy barriers separating the two states. We have estimated this barrier from the orientational probability distribution, $p(\cos\phi)$,

$$p(x) = \langle \delta(\cos\phi - x) \rangle = \frac{\int d\Gamma \delta(\cos\phi - x) \exp[-\beta U(\mathbf{r})]}{\int d\Gamma \exp[-\beta U(\mathbf{r})]} \quad (11)$$

computed over long Monte Carlo simulations, typically involving about 5×10^5 steps. The free energy ‘landscape’ associated to the orientation of the nanoparticle at the liquid-liquid interface can be obtained from the normalized distribution, $p^*(x)$, through, $\beta F(x) = -\ln(p^*(x))$.

Figure 2 shows the corresponding free energy function. Two minima are clearly visible, separated by a free energy barrier of $\approx 0.3k_B T$, which provides an estimate for small nanoparticles (≈ 3 nm) at interfaces with typical interfacial tension of ≈ 15 mN/m. The energy barrier is small, emphasizing the relevance of thermal fluctuations in determining the physics of these small systems. It is important to note that the height of the energy barrier can be tuned in a number of ways. According to the theory we can either change the nanoparticle size, or the interfacial surface tension. For a nanoparticle with a typical size of 2 nm, an increase in the surface tension (e.g. oil-water interface 50 mN/m) would increase the activation energy up to $2.5k_B T$. Large particles increase dramatically the activation energies, e.g., for nanoparticles at the water-air interface, the activation energies increases up to $\approx 20k_B T$ for 5 nm and $\approx 300k_B T$ for 20 nm size particles.

Size effects can be investigated through the analysis of nanoparticles with different size but with the same aspect

ratio. Figure 2 compares the orientation of two nanoparticles with sizes $\sigma_{\parallel}/\sigma = 8, \sigma_{\perp}/\sigma = 4.8$ and $\sigma_{\parallel}/\sigma = 5, \sigma_{\perp}/\sigma = 3$. The minor axis of the smaller nanoparticles is of the same order as the interfacial gap. Our results suggests a small dependence of the orientation with nanoparticle size, although for such small particles the fluctuations become significant (cf. Fig. 2). We expect that the thermodynamic description of even smaller particles will break down. Therefore one should be cautious in interpreting possible variations in the orientation behavior in terms of interfacial forces alone, e.g., line tensions.

The dependence of the orientation with nanoparticle anisotropy can also be conveniently addressed within the thermodynamic model. The main prediction of the theory is that the energy field required to rotate the nanoparticle to a given angle, increases with nanoparticle anisotropy. Such dependence is confirmed by the numerical simulations (cf. Figure 3). Nanoparticles with small anisotropy ($\alpha = 1.2$) require smaller energy in order to impinge a change in their orientation. In the limit of a spherical particle, $\alpha = 1$, the reorientation with the external field would be instantaneous, since the rotation of the nanoparticle does not cost interfacial free energy. Again for the field strengths investigated here, the theory shows a quantitative agreement with the simulation results.

In the model above we assumed that the surface tensions of the nanoparticle with phases 1 and 2 are the same, $\gamma_{p1} = \gamma_{p2}$. This was achieved by setting a common nanoparticle-liquid interaction strength, $\epsilon_{p1} = \epsilon_{p2} = 1.5$. In this situation the thermodynamic model shows that

Fig. 3. Orientation of anisotropic nanoparticles with the external field. Circles and plus symbol, $\sigma_{\parallel}/\sigma = 8.4, \sigma_{\perp}/\sigma = 7$,

Fig. 4. Normalized density profile of the liquid around the anisotropic nanoparticle for different interactions strengths $\sigma_{\parallel}/\sigma = 8.4, \sigma_{\perp}/\sigma = 7$.

the fluid-nanoparticle interactions do not play any role in determining the orientation of the nanoparticle (see equation 6). Nonetheless from a microscopic perspective the local structure of the liquid around the nanoparticle is modified by the interaction strength. This effect is

well illustrated in the liquid density profiles around the nanoparticle (cf. Fig.4), which shows that weak interaction strengths result in a significant loss in the structure of the solvation layer. Our simulation results (see Figure 3) show that the nanoparticle behavior is rather insensitive to the nanoparticle-fluid interaction strength, and consequently to the microscopic structure of the solvation layer. This result is in agreement with the thermodynamic model.

5 Summary

Thermodynamics offers a theoretical approach to investigate the behavior of nanometer size particles at fluid interfaces. We have addressed the applicability of thermodynamic theories to investigate the complex interfacial behavior of non-spherical nanoparticles at liquid-liquid interfaces. The nanoparticles interact with external fields through an embedded permanent dipole moment. The external field induces the nanoparticle rotation. This set up is of interest to self assembly of nanoparticles as well as design of interfacial devices, e.g., sensors, which are sensitive to variations in the interfacial free energies. We have shown that a thermodynamic theory defined in terms of a few material properties (surface tensions, particle geometry) is able to provide an accurate account of the behavior of truly nanosized particles in a wide range of conditions; nanoparticle-solvent interactions strength, nanoparticle size and nanoparticle anisotropy. Hence, thermodynamic theories reveal themselves as powerful approaches to investigate interfacial behavior at the nanoscale at a

quantitative level, and possibly help in the interpretation of future experimental studies.

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