

Electric-Field Induced Phase Transitions of Dielectric Colloids : Impact of Multiparticle Effects



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ABSTRACT

The thermodynamic framework for predicting the electric-field induced fluid like-solid like phase transition of dielectric colloids developed by Khusid and Acrivos [Phys. Rev. E. 54, 5428 (1996)] is extended to examine the impact of multiscattering/multiparticle effects on the resulting phase diagrams. This was accomplished using effective permittivity models suitable both over the entire composition region for hard spheres ($0 \leq c < c_{\max}$) and for multiple types of solid packing structures (random close-packed structure, FCC, BCC). The Sihvola-Kong model and the self-consistent permittivity model of Sen *et al.* [Geophysics 46, 781 (1981)] were used to generate the coexistence (slow phase transition) and spinodal (rapid phase transition) boundaries for the system and compared to assuming Maxwell-Garnett permittivity. It was found that for larger dielectric contrasts between medium and particle that the impact of accounting for multiscattering effects increased and that there was a significant shift in the resulting phase diagrams. Results obtained for model colloidal systems of silica-dimethylsulfoxide and silica-isopropanol showed that critical electric field strength required for phase transitions could rise by up to approximately 20% when considering multiparticle effects versus the isolated dipole case. The impact of multiparticle effects on the phase diagrams was not only limited purely to the direct effect of volume fraction on permittivity and particle dipoles but also on the curvature of the volume fraction dependence. This work stresses the importance of accounting for particle effects on the polarization of colloidal suspensions, which has large implications for predicting the behavior of electro rheological fluids and other electric-field driven phenomena.

Keywords : Silica-Dimethylsulfoxide, DMSO, Polystyrene Colloidal Crystals

The phenomena of electric field induced phase transitions of colloidal suspensions are a well-established field, with many interesting applications. Electric fields have been used to drive colloidal crystal formation with lattice structures not normally obtainable via other methods for templating colloidal crystals and other transitions of interest. These lattice structures include colloidal martensite (body-centered tetragonal lattice) from refractive index matched silicadimethylsulfoxide (DMSO)-water suspensions, large scale polystyrene colloidal crystals in aqueous suspension and drive the phase transition and aligned block copolymer micelles.¹⁻⁵ Additionally, these types of phase transitions also govern electrorheological (ER) fluids, where the phase transition of the suspended solid phase into a more concentrated form causes a large shift in the rheological behavior (viscosity).⁶ More specifically, particles in the suspension can align into chains (1d analog of 2d colloidal crystals) and this chaining behavior can significantly impact the viscosity in a system.

Conclusion

To predict the phase transition, a number of different frameworks have been approached from continuum mechanics, molecular/Brownian dynamics type approach to solve for the motion of individual particles to treating the pattern formation in terms of the classic Ginzburg-Landau function and solving for concentration profiles by variational principles.

CONCLUSIONS Electric-field induced phase transitions of dielectric colloids were predicted using an extension of a thermodynamic framework previously developed by Khusid and Acrivos. This framework treats the free energy of a suspension as having two primary contributions, entropic, and electric. Entropic contributions are treated in a hard-sphere manner, with the suspension compressibility assumed to follow the Carnahan-Starling equation of state. Electrical contributions are accounted for using the average electrical energy of a non-conducting suspension from continuum electrodynamics. The influence of multiscattering (volume fraction) effects on the resulting coexistence and spinodal lines of non-conducting suspensions was examined through use of two effective permittivity models, the Sihvola-Kong formulation and the self-consistent permittivity model of Sen et al.

Accounting for multiparticle effects on suspension permittivity causes a significant shift in the behavior of the derivatives of permittivity with respect to volume fraction. This shift leads to large changes in the chemical potential and osmotic pressure, which leads to shifts in the coexistence and spinodal lines and the critical concentration and field strength for electric-field induced phase transitions. More specifically, increasing the value of the Sihvola-Kong parameter from 0 (Maxwell-Garnett model) leads to an increase in the critical concentration and field strength for aggregation, as well as a decrease in the overall region of coexistence and spinodal transitions. The behavior of the different permittivity models was not completely 1:1 with their respective magnitudes in permittivity, the derivatives of these functions played a large role in determining the magnitude of coexistence and spinodal line shifts. The Sen et al. self-consistent permittivity model was found to predict a positive, monotonically increasing value for $d\epsilon/d\phi$ while the values obtained when using the Sihvola-Kong model with a $\frac{1}{4} \leq \alpha \leq 3$ are monotonically decreasing, starting off positive but becoming negative at higher volume fractions. This leads to the interesting shift in the critical concentration versus critical electric field strength between these two models, where the Sihvola-Kong predicts a higher critical concentration but a lower critical electric field strength. Similarly, $d^2\epsilon/d\phi^2$ is found to be positive and monotonically decreasing when using the Maxwell-Garnett formulation but is positive and monotonically increasing for the Sen et al. model, while it is not necessarily monotonic depending on the choice of Sihvola-Kong parameter. This affects the resulting spinodal.

Lines, determining the boundary between slow and fast aggregation. This framework is not limited to the permittivity models chosen for this work but is generally applicable to use with any effective permittivity model, as long as the suspension is non-conducting. Extension to include conductivity effects, in the form of both volume-fraction dependent and nonlinear conductivity behavior at high electric field strengths, along with the volume-fraction dependent permittivity is desirable as it would be suitable for predicting properties of interest in colloidal phase transition studies, as well as electrorheology work, and this is the subject of ongoing investigations

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