



PhD Executive Summary

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Thesis Title: “Development of Self-Consistent Field Theory Models for Predicting the Structure and Properties of Inhomogeneous Polymer Systems: Application in Nanocomposite Materials”

The main goal of this PhD was to develop a generic theoretical model based on *Self-Consistent Field theory* (SCFT) to predict the structural and thermodynamic properties of solid-polymer interfaces. In particular, we were interested in systems where the solid surfaces are chemically grafted with polymer chains. In the context of the thesis, the solids are of planar or spherical geometry (nanoparticles, NPs), immersed in a polymer matrix or in contact with vacuum, and the grafted chains are chemically identical to those of the matrix.

When conducting SCFT calculations, the primary task is to solve the *Edwards* diffusion equation. This is a time-dependent partial differential equation (PDE), whose solution is the *restricted partition function*, i.e., a quantity proportional to the probability density that a segment at specific contour length from the start of a chain will occupy a certain position in space. In our case, the numerical solution of this PDE is performed via a custom-made in-house code named *RuSseL*. The one-dimensional version of the code applies a *Finite Differences* (FD) scheme, while the three-dimensional version is based on the *Finite Element Method* (FEM). The 1D version is considerably faster than its 3D analogue, but it is restricted in specific types of geometries, i.e., single planar interface, opposing planar interfaces and a single spherical nanoparticle. Furthermore, in these 1D models, all grafting points degenerate into a single point of the 1D space; this is usually called the *smearing approximation*. Despite its restrictions and approximations, the 1D model is quite useful, because it serves as an extremely fast testing tool for the development of new features and functionality. On the other hand, the 3D model can be applied in systems of arbitrary geometry and any kind of boundary conditions (i.e., *Neumann*, *Dirichlet*, *periodic*).

The first system we addressed was a single polystyrene-grafted silica nanoparticle embedded in polystyrene melt at infinite dilution. The density profiles of matrix and grafted chains, along with additional structural characteristics such as the chain shape, profiles of middle/end segments and adsorbed/free segments were derived for various particle radii, lengths of grafted chains and grafting densities. The free energy of the system was also derived for the same parameters. We have estimated the thickness of the grafted brush across the whole range of parameters, and compared our results with

experimental findings and scaling laws reported in the literature, namely, the *Daoud and Cotton* model, which was originally derived to describe the behavior of star polymers. We showed that this model is able to accurately describe the scaling of the brush only if the radius of the NP is in the range of 4-8 nm. When the radius of the NP is varied outside this domain, the exponents of the *Daoud and Cotton* model need to be adjusted. We have proposed a correlation for those exponents with respect to the NP radius and the pre-exponential factor appearing in the scaling law, which offers a satisfactory prediction of the size of the brush for a broad range of particle radii. Nonetheless, this correlation/law describes accurately the size of the brush when the system finds itself in the dense brush regime. In the *mushroom* regime, the size of the brush exhibits a weak dependence on the grafting density and particle radius and was found to be proportional to the square root of the molecular weight of the grafted chains.

Concerning the free energy of the same system, we decomposed it into separate terms associated with the cohesive segment interactions, the field, the solid-polymer interactions, translational entropy of matrix chains, and configurational entropy of grafted chains. The term of highest interest was the one related to the entropy of grafted chains and we have quantified the free energy cost which arises due to the reduction of available chain conformations, and therefore entropy, when the grafting density or chain length increases. The curvature of the particle is an important parameter; when the particles are smaller, at given areal density, there is more room for the grafted chains to develop their conformations near the particle surface before they start stretching towards the bulk polymer region. When the latter happens, it is harder for matrix chain segments to penetrate into the interfacial region and interact with the solid surface. The entropic term of grafted chains dominates the free energy of the system for high grafting density and grafted chain length. It was further decomposed into a part related to the field and another one which is purely related to chain stretching. The latter was assessed and compared to predictions obtained via the *Alexander* model for incompressible brushes. The SCFT and *Alexander* models agreed in describing the stretching of grafted chains in the limit of large grafting densities.

We went a step further and investigated the structural and thermodynamics properties of polystyrene chains grafted on a single silica NP, when the latter is in contact with vacuum, i.e., no matrix chains exist in the system. The first observation that one makes when removing the melt from such a system is that the density profiles of grafted chain segments collapse towards the surface of the solid. This is a consequence of two factors: first the response of grafted chain segments to the potential exerted by the solid and, most importantly, the fact that vacuum is equivalent to a bad solvent, i.e., grafted chain segments tend to stick together in vacuum. In terms of free energy, in the absence of matrix chains, the system was described in the canonical ensemble, in contrast to the case where polymer melt was present, where a grand canonical formulation was adopted for the matrix chains. The difference in the free energy of the two systems (in presence and absence of polymer melt) allowed us to estimate the *solvation Gibbs energy* as a function of the grafting density, intensity of solid-polymer interactions, particle size, and lengths of grafted and matrix chains.

One of the key findings of this study was that NP solvation can indeed be accurately predicted via experimentally measured thermodynamic quantities, when the amount of grafted material is very low or very high; it is directly related to the adhesion tension between the bare particle and the matrix or the surface tension of the grafted polymer, respectively. However, when the amount of grafted polymer assumes intermediate values (depending on the curvature of the particle), one must perform theoretical calculations (in our case with SCFT), experiments, or simulations to obtain accurate results. This happens because in these intermediate cases, the dependence of solvation free energy on molecular characteristics is not governed by enthalpic interactions, but the entropy of grafted chains, in both the melt and vacuum

interfaces, affects the free energy of each system, especially for larger particles. Based on the findings of this work, we suggested a model for the estimation of the solvation free energy of a NP as a function of the particle size and the amount of grafted polymer. This model involves experimentally measured polymer properties and is expected to work in cases of matrices that are chemically dissimilar to the matrix chains too. This is quite important, since being able to predict the relative tendency of a grafted-NP to dissolve in two different polymer matrices, is exactly what one needs in order to estimate the partition coefficient of the NP and therefore determine its equilibrium distribution between the two matrices.

Next, we implemented our SCFT model in a system of two opposing polystyrene-grafted silica plates to derive the *potential of mean force* (PMF), i.e., the free energy of the system as a function of the plate-to-plate distance. This system is mathematically equivalent to one containing two grafted particles of extremely large particle radius. The PMF was derived as a function of the length of grafted chains, grafting density and intensity of solid-polymer interactions. In addition, we allowed the two plates to be grafted with different numbers and/or lengths of grafted chains, in order to investigate the impact of grafting asymmetries on the PMF and therefore stability of the nanocomposite system. Such asymmetries are expected to occur when these systems are prepared experimentally. In all cases, we also calculated the PMF between the two brushes in the absence of melt chains by applying again a canonical ensemble formulation.

For the case of opposing grafted surfaces in contact with melt, we found that, with decreasing molecular weight of matrix chains, the solvent conditions for the grafted chains are enhanced, which practically means that grafted chains prefer to interact with matrix chains than with themselves. The result of this behavior is that the PMF between the two grafted plates becomes repulsive. The opposite trend is observed when matrix chains become longer than the grafted chains. Until a certain point, asymmetries in grafting density or grafted chain length are not capable of destabilizing the system; only when both of these parameters have large deviations between the two plates, can the PMF exhibit an attractive well. This implies that there is some room for asymmetry in experiments without destroying stability. The polymer affinity to the solid surfaces appears to have a minor effect on the PMF. So does the equation of state (in our case Helfand or Sanchez-Lacombe) that one uses to describe nonbonded interactions between segments. Based on our calculations, we identified and visualized a region in the parameter space (grafting density of each plate, length of grafted chains of each plate, length of matrix chains) where the system of the two surfaces is stabilized.

For the system of the two opposing grafted surfaces in contact with vacuum, an interesting observation was that, below a critical plate-plate distance, the PMF decreased abruptly, indicating the manifestation of a phase transition where the adjacent brushes interpenetrate and form a single film in the central region of the system. In addition, low density regions were formed in the vicinity of the solid surface, indicating that the brushes have been stretched significantly to form this “film” region. The manifestation of the phase transition depends on an interplay among three dominant factors: an enthalpic gain due to the lower surface area of the merged brushes, an enthalpic loss due to the detachment of the grafted film from the solid surface, and a conformational penalty due to chain stretching.

One of the accomplishments of this PhD is that we can perform all these calculations in three-dimensions with the FEM version of *RuSseL*, which is going to be published soon and publicly available, as has happened with the one-dimensional version, so that anyone can reproduce our results, contribute to the development of the code and/or use it for their own purposes. This 3D implementation avoids any smearing of the grafting points, normal or parallel to the solid surfaces. We undertook detailed

benchmarks on a system of a single nanoparticle immersed in polymer melt and performed a direct comparison between 1D- and 3D-SCFT calculations over a broad range of parameters in order to assess the validity of the smearing approximation in terms of both chain structure and system thermodynamics.

By constructing three-dimensional plots of segments belonging to grafted chains, we are able to visualize the cloud of segments around the solid surface and illustrate the transition from the mushroom to the swollen-brush regime. Furthermore, taking advantage of the 3D nature of the model and the absence of smearing in the initial conditions applied at the grafting points, we derive and plot in 3D the density profile of segments belonging to a specific grafted chain, as one would do in a particle-based simulation. Most importantly, we are able to impose a variety of irregular grafting distributions on the solid surfaces using a Monte-Carlo sampling scheme to generate the grafting points of the surface. We have shown that different grafting distributions result in variations in brush thickness and free energy relative to the case of equidistant grafting, which is the most usual assumption when performing such calculations. Adding the grafting distribution to the degrees of freedom involved in the computational design of polymer-grafted nanoparticle systems takes us closer to experimental practice and to nanocomposites with tailor-made self-assembly properties. In this spirit, we have also determined the PMF between two spherical polystyrene-grafted silica nanoparticles embedded in polystyrene matrix for various grafting distributions of the particle surfaces. The radius of the particle and average grafting density was constant; for each grafting distribution, we varied the matrix-to-grafted chain length ratio.

In order to have the ability to run 3D-SCFT calculations on multi-nanoparticle systems in the absence or presence of polymer matrix, we have added the functionality of imposing periodic boundary conditions when the solution of Edwards PDE takes place. The user can now insert any (reasonable) number of grafted nanoparticles inside the periodic box, arranged on a crystal or amorphous structure, and run SCFT calculations, as he/she would do in a particle-based simulation.

Publications that have resulted from this thesis so far (in chronological order):

- C. J. Revelas, A. P. Sgouros, A. T. Lakkas, D. N. Theodorou, “Addressing Nanocomposite Systems via 3D-SCFT: Assessment of Smearing Approximation and Irregular Grafting Distributions”, *Macromolecules*, 2023, 56, 4, 1731-1746
- A. P. Sgouros, C. J. Revelas, A. T. Lakkas, D. N. Theodorou, “Solvation Free Energy of Dilute Grafted (Nano)Particles in Polymer Melts via the Self-Consistent Field Theory”, *The Journal of Physical Chemistry B*, 2022, 126, 7454-7474, DOI: **10.1021/acs.jpcc.2c05306**
- C. J. Revelas, A. P. Sgouros, A. T. Lakkas, D. N. Theodorou, “RuSseL: A Self-Consistent Field Theory Code for Inhomogeneous Polymer Interphases”, *Computation*, 2021, 9, 57, DOI: **10.3390/computation9050057**
- A. P. Sgouros, C. J. Revelas, A. T. Lakkas, D. N. Theodorou, “Potential of Mean Force between Bare or Grafted Silica/Polystyrene Surfaces from Self-Consistent Field Theory”, *Polymers*, 2021, 13, 1197, DOI: **10.3390/polym13081197**
- A. T. Lakkas, A. P. Sgouros, C. J. Revelas, D. N. Theodorou, “Structure and Thermodynamics of Grafted Silica/Polystyrene Nanocomposites Investigated Through Self-Consistent Field Theory”, *Soft Matter*, 2021, 17, 4077-4094, DOI: **10.1039/d1sm00078k**
- C. J. Revelas, A. P. Sgouros, A. T. Lakkas, D. N. Theodorou, “A Three-Dimensional Finite Element Methodology for Addressing Heterogeneous Polymer Systems with Simulations Based on Self-Consistent Field Theory”, *International Conference of Computational Methods in Science and Engineering 2020 (ICCMSE 2020)*, 2021, DOI: **10.1063/5.0047729**