Long-range repulsion in polymer melts: Does the Anti-Casimir effect exist ?

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Background: In quantum field theory, the Casimir effect is a physical force, acting on the macroscopic boundaries of a confined space, which arises from the quantum fluctuations of the field. Named after the Dutch physicist Hendrik Casimir, who introduced the effect in 1948 focusing on electromagnetic systems [1], it is closely related to the London–van der Waals force [2] which can be formulated on the same footing. Importantly, the (generalized) Casimir forces as the other (classical) contributions [2] to the van der Waals force are always attractive which leads, e.g., to the well-known aggregation of small colloidal particles in solvents. Interestingly, recent theoretical work [3] of our research group at the ICS suggests that universal long-range interactions exist in dense solutions and melts of linear polymer [4] that are directly opposite to the van der Waals attraction and it was argued that this Anti-Casimir effect may increase the stability of colloids in dense polymer solutions.

Bond-fluctuation model study of bulk correlations: As one important consequence it was found that the pair correlation function of all monomers of the melt should follow at large distances a power law, rather than the exponential decay predicted by Edwards [4,5] based on Flory's ideality hypothesis, and a corresponding relation in reciprocal space for the (experimentally relevant) total structure factor. In the first part of the proposed PhD project we shall attempt to demonstrate numerically the existence and relevance of the Anti-Casimir effect for equilibrium polymer systems with and without closed loops by means of the Monte Carlo simulations of the bond-fluctuation model using soft monomers and allowing the chains to freely break and recombine.

Bead-spring model simulations of slit geometry: The second part of the PhD will focus on the pressure difference of a polymer melt confined in a thin slit of width H in grand-canonical contact with a large reservoir. While for equilibrium polymer melts with loops the density and pressure differences inside and outside the slit must vanish they should become finite for linear chain systems according to theory. We shall investigate the predictions for soft equilibrium polymers (with and without closed loops) by means of the LAMMPS programming environment [6].

In a nutshell: Motivated by recent polymer field theoretical work we suggest a mainly computational PhD study on equilibrium polymer melts with soft excluded volume.

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