

Computing polymer diffusio-phoretic mobilities

S. Ramírez-Hinestrosa^{1*}, H. Yoshida², L. Bocquet³, D. Frenkel¹

¹Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, United Kingdom

²Toyota Central R&D Labs., Inc., Nagakute, Aichi 480-1192, Japan

³LPS, UMR CNRS 8550, École Normale Supérieure, 24 Rue Lhomond, 75005 Paris, France

*sr802@cam.ac.uk

We use non-equilibrium molecular dynamics to simulate the transport of a polymer in a binary solution on which we have imposed a concentration gradient. We compute the phoretic mobilities for different interaction strengths between the polymer and the solute, and we study the variations of the phoretic mobility when the polymer length is changed. An interesting finding of this work shows that the mobility has a non-monotonic dependence on the strength of the interaction between the polymer and the solution. This insight can be used to optimise diffusio-phoretic transport in experiments.

1 Introduction

A gradient in the chemical potential of the components in a fluid mixture causes a net hydrodynamic flow in the presence of an interface that interacts differently with the various components of the mixture.

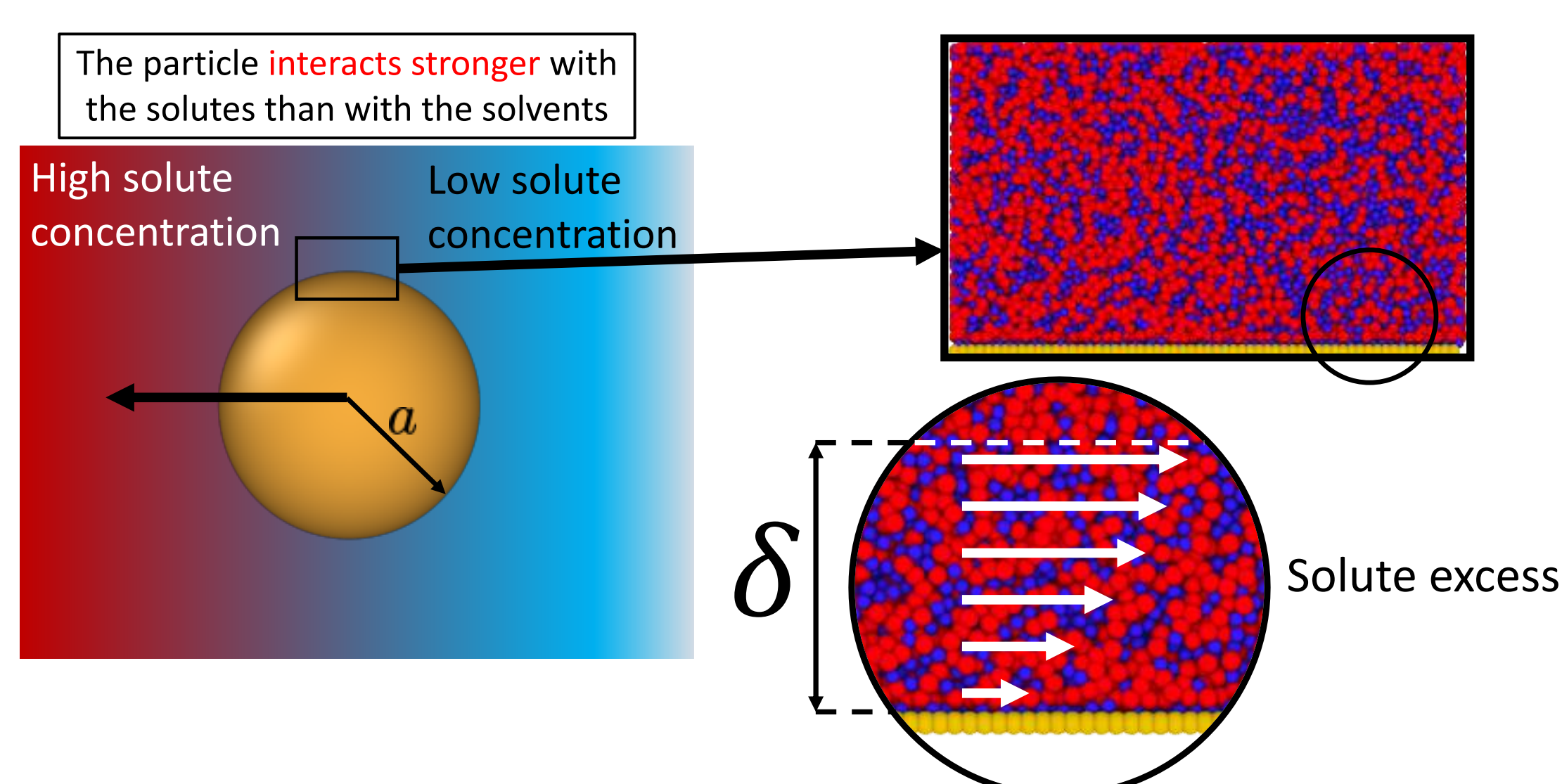


Figure 1: The origin of diffusio-phoresis at the interface with length δ

Diffusio-phoresis of polymers is different from that of simpler structures, as colloids:

- Polymers have a fluctuating shape and an intrinsically fuzzy surface.
- Particles that are subjected to phoresis are not large compared to the range of adsorption/depletion δ .
- Hydrodynamic flow fields can penetrate the outer fuzzy layer of the polymer.
- Solutes can diffuse through the polymer.
- Strongly binding solute may result in the collapse of the polymer
- Conformational changes affect mobility.

2 Field-driven simulations

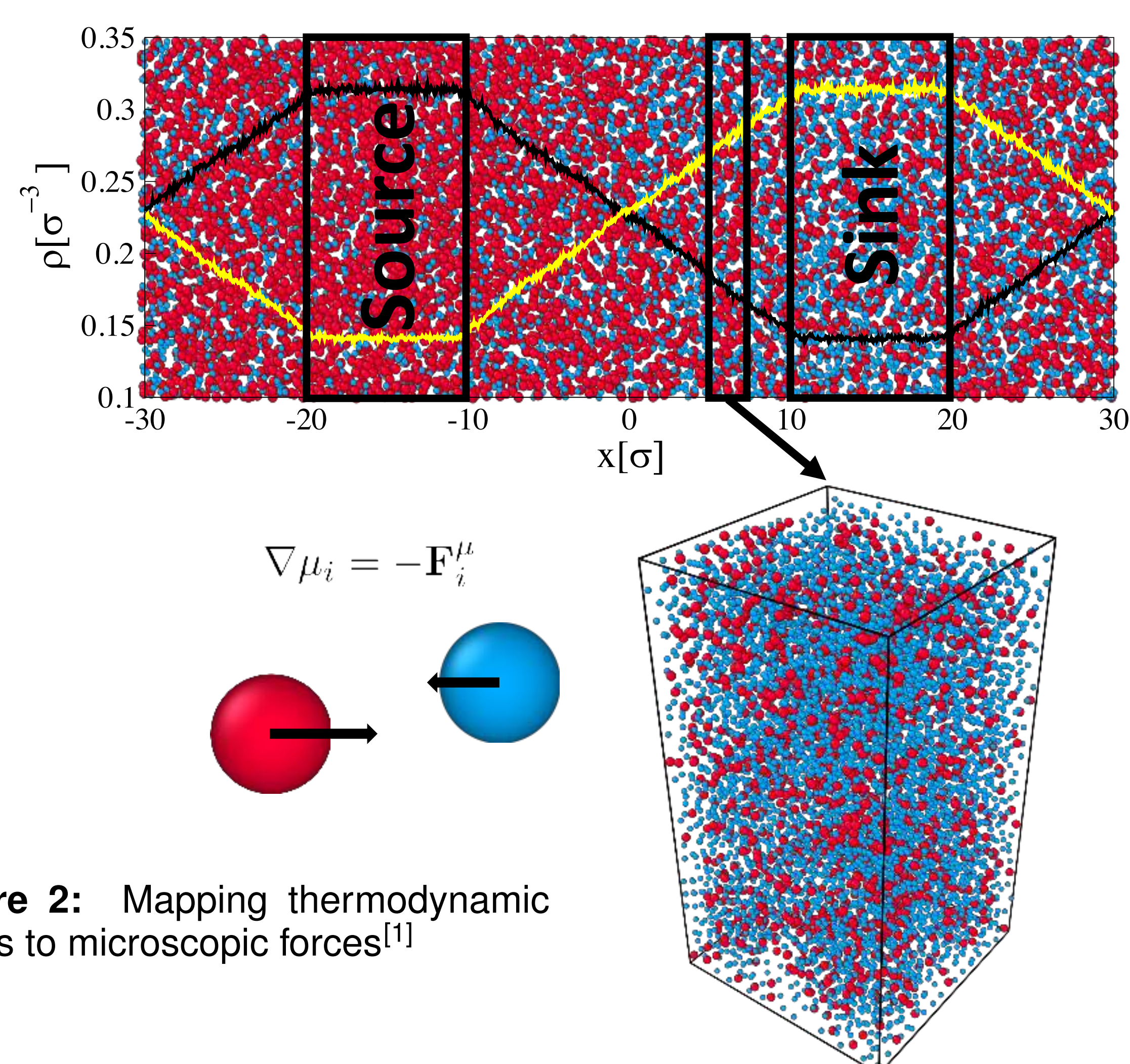


Figure 2: Mapping thermodynamic forces to microscopic forces^[1]

3 The system

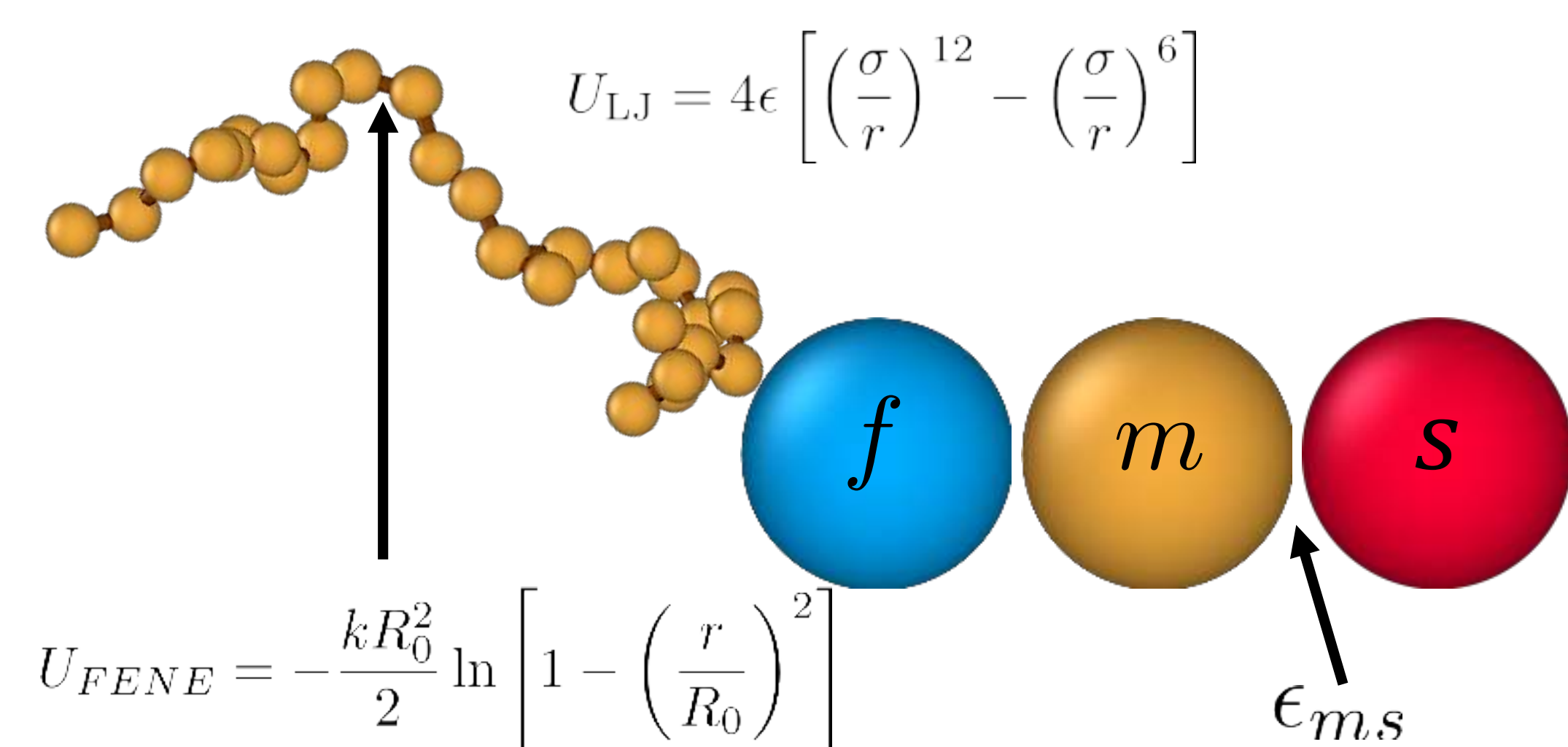


Figure 3: Interactions between particles. ϵ_{ms} is varied to change the monomer-solute interaction.

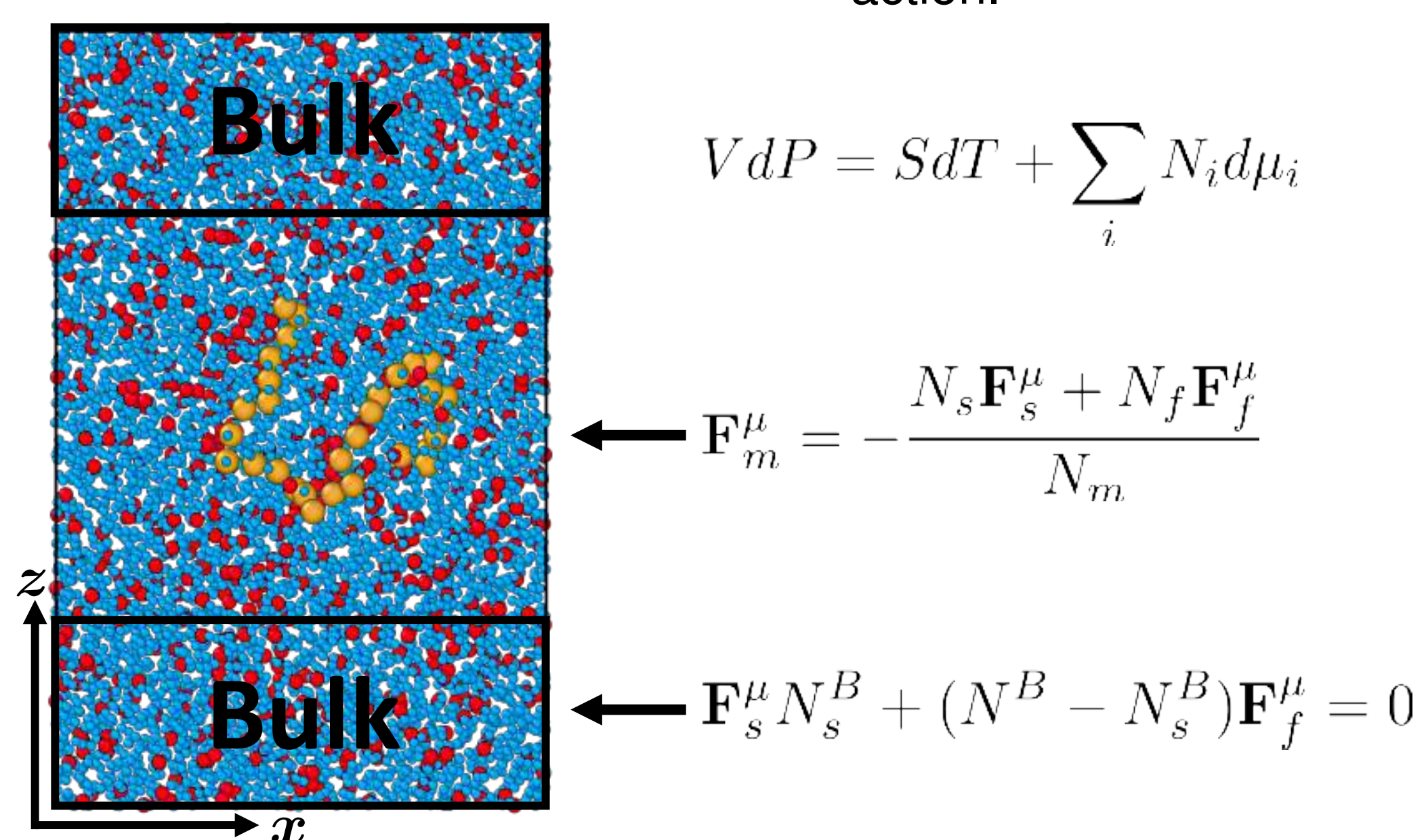


Figure 4: Application of the microscopic forces in the system

4 Results^[2]

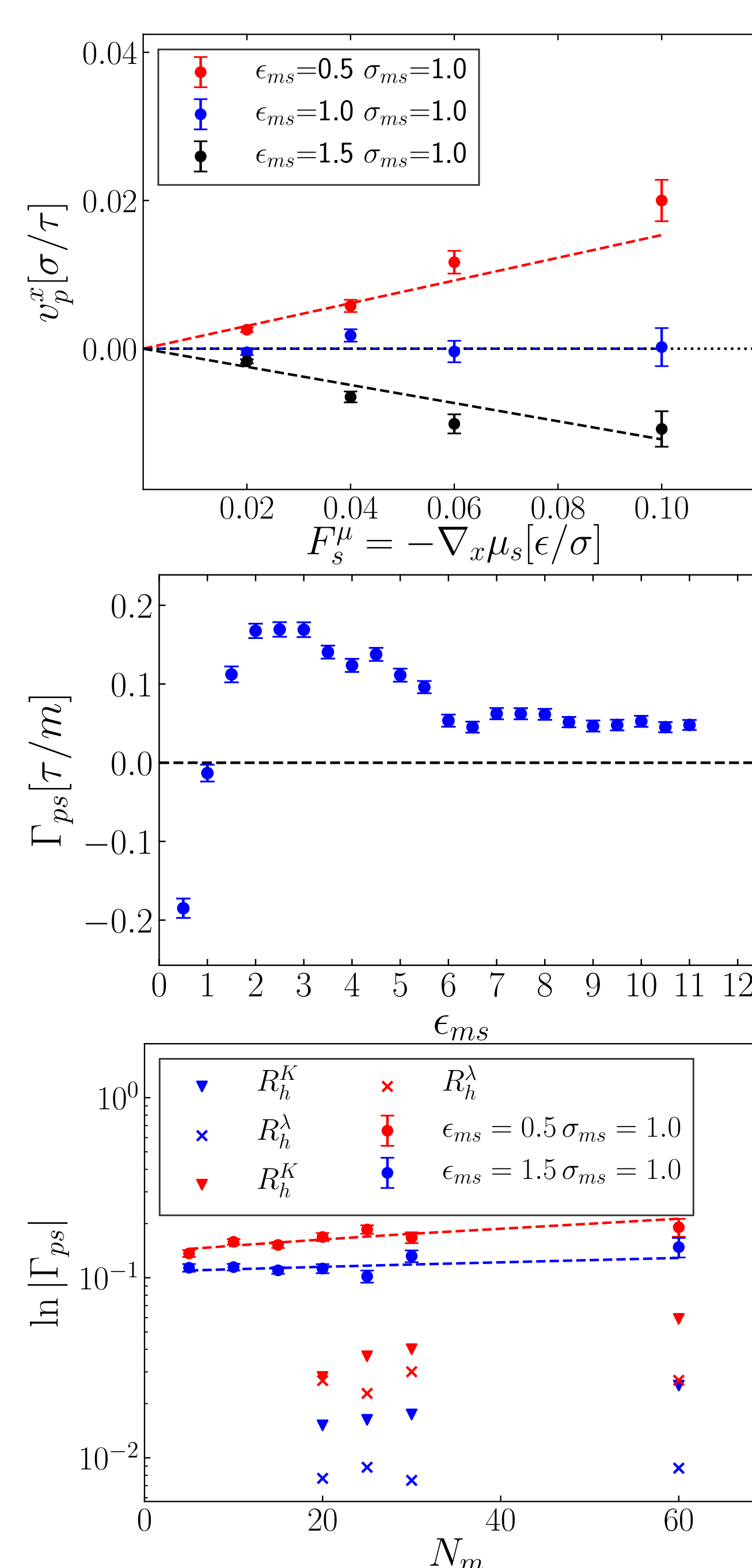


Figure 5: Polymer velocities in the direction of the gradient for different LJ interactions ($\epsilon_{ms}, \sigma_{ms}$) vs the force applied on the solute particles

Figure 6: Phoretic mobility $\Gamma_{ps} = v_p^x / \nabla_x \mu_s$ as a function of the interaction between the monomers and the solutes ϵ_{ms}

Figure 7: Phoretic mobilities Γ_{ps} vs the number of monomers in the polymer N . Theoretical results^[3] are shown for two different estimations of the hydrodynamic radius: R_h^K is the Kirkwood's approximation and R_h^λ are the results obtained by using Stokes-Einstein equation