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Molecular Dynamics Simulations
for Anisotropic Systems

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9.1 Introduction

By using conventional molecular dynamics (MD) methods, it is often difficult to properly simulate anisotropic systems. This is because the imaginative boundaries under periodic boundary conditions, i.e., the simulation cell, do not obey the correct dynamics of the system which originate from the dynamics of the molecules inside them. Periodic boundary condition is a clever tool to avoid simulating the whole size and substituting with a part of it. However, in anisotropic systems, periodic boundaries must be used with an appropriate cell dynamics to avoid artifacts induced by them.

9.2 Simulation Cells with Anisotropic Shape

A simple case is when the volume of the system we would like to simulate is not cubic but has an anisotropic shape. If we simulate a system in an elongated cell using the Parinello and Rahman (P&R) method [1], the fluctuation of the cell length will differ for the same value of piston mass in all directions (see Fig. 9.1 of [2]) which is a consequence of the P&R method not satisfying the virial theorem. This makes the quality of statistics for a fixed time range quite different in each direction because of the different period of fluctuation. The original P&R method has been modified to satisfy the virial theorem by introducing a different dynamics in the simulation cell [2]. This makes it possible to simulate even strongly anisotropic systems by a single piston mass.

9.3 Simulating Anisotropic Liquids

Much more difficulty arise when the source of anisotropy is not external (comes for the simulation cell) but also internal as well. Liquid crystal phases are a
state of matter were the physical properties are anisotropic. In lipid membrane, anisotropy and complexity appear in many different scales from the constituent molecules up to the systematic structure as an interface. In such systems, anisotropy in both space and time scale appear as a spontaneous consequence of the dynamics of the molecules inside the simulation cell. In contrast to crystals, smectic liquid crystals and lipid membranes posses elasticity but only in the direction normal to the layers. The layer itself is liquid and only elastic under uniform compressive force. As liquids need a container to avoid spreading out, liquid crystals also need some support in the direction parallel to the layers to maintain the number of smectic layers. The layer thickness compressibility depend on temperature, changing especially drastically near the phase transitions [3]. There is also a large difference in the time scales of fluctuations parallel and perpendicular to the layers in these systems. The temperature dependence of the layer thickness requires the simulation cell to change its shape not matching the periodicity in the fixed cell shape of constant volume or Andersen’s constant pressure method [4]. When the cell shape doesn’t match the internal periodicity of the system, stress is induced to the system and uniform hydrostatic pressure is not achieved. The absence of elasticity in the direction parallel to the layers results in a large strain fluctuation in this direction, thus leading to the divergence of cell length in the P&R method [1]. In other words, the cell is too flexible in the P&R method to avoid the anisotropic soft matter from spreading out. We need a cell dynamics which can retain the shape to a certain degree but still flexible enough to allow the the anisotropic change in the shape of cell without causing any stress inside the system.

We have achieved this by introducing an anisotropic factor $\alpha$ of the simulation cell in the appropriate Lagrangian of the system [5]. The choice of an appropriate cell variable and cell dynamics (kinetic energy of the simulation cell in the Lagrangian) is the key to get successful simulation results in anisotropic systems.

9.4 Simulations under Constant Surface Tension

Similar problems, such as continuous expansion or contraction of the cell lengths observed in simulating anisotropic liquids, occur in simulating liquid-liquid interfaces. In systems of liquid-liquid interface, due to the interface (and the anisotropy of the composite liquids), there exists large differences in visco-elastic properties depending on the direction (along and normal to the interface) which lead to expansion or contraction of cell lengths (see for instance Fig. 5 in [6]). This is due to the simulation cell dynamics of the methods used where the cell dynamics is described by the equation of motions of each cell lengths. We introduce the anisotropic factor $\alpha$ of the simulation cell along with the surface area to describe the dynamics of the cell [7,8]. The