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Order–disorder structural transition in a confined fluid

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HIGHLIGHTS

- The analysis of the amorphous/solid to disordered liquid structural phase transitions of an anomalous confined fluid.
- The fractal dimension as a quantitative measure to describe structural transitions.
- Structural configuration of particles interacting through a two-length scales potential confined by two infinite plates.
- The mapping reported show that the fractal dimension increases with the density and with the temperature.

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ABSTRACT

In this paper we analyze the amorphous/solid to disordered liquid structural phase transitions of an anomalous confined fluid in terms of their fractal dimensions. The model studied is composed by particles interaction through a two-length scales potential confined by two infinite plates. This fluid that in the bulk exhibits water-like anomalies under confinement forms layers of particles. We show that the fluid at the contact layer forms at high densities structures and transitions that can be mapped into fractal dimensions. The multi-fractal singularity spectrum is obtained in all these cases and it is used as the order parameter to quantify the structural transitions for each stage on the confined liquid. This mapping shows that the fractal dimension increases with the density and with the temperature.

1. Introduction

The characterization of the phases present in complex system is not trivial. Usually it depends in identifying the correct order parameter of the structure. For instance, the structural transformation by thermal or mechanical perturbation of fibrous, dendritic, or colloidal configurations, formed by aggregation or reaction processes have been quantified from different measures of complexity. One of these measures is the fractal dimension. The fractality is a geometrical, topological and structural property present in many natural physics or simulated complex systems [1–3]. In many cases a fractal structure results from the kinetic aggregation of a group of particles or from the reaction processes between them [1,4,5] in a process that resembles a very slow nucleation and growth of mechanism. This is visually manifested by different final distributions of the particles that entail universal properties, and also influence the physical, biological or chemical properties on the system [4–9]. These distributions can also be quantified by the mass fractal dimension that is a measure employed to quantify the different structural phase transition [10–12].

In a number of systems, a single fractal dimension is unable to capture the full complexity of the system. The multi-fractal spectrum describes the scaling correlations, coexisting in the dynamical evolution of the system, at different length scales

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of observation. It is employed to provide a description of the aggregation kinetics. It also gives the information about how the new phase reaches the equilibrium state [3,13,14]. In this way the measure of the microscopic multi-scale structure through the local fractal dimension is an important tool to identify the macroscopic state of the system, which influences the physical emergent properties.

Then, the fractal dimensions can be used as an additional tool for characterizing the complex phases emerging from phase transitions. This strategy was employed in the study of rheological fluids [15,16], granular materials [7,17,18], magnetic wall domains in boracite [19] and other complex systems [11,20,21]. In the case of rheological systems, the final structures obtained by magnetic particles dispersed in mineral oils and perturbed by magnetic fields show different degrees of order that were quantified by its mass fractal dimension [15]. This result was also checked experimentally [15,17]. This structural transformation can be analyzed by glass transition approach [22–24] and is possible to identify the liquid-glass and the liquid-crystal phase transition.

All the examples cited above in which the fractal analysis were used to identify new phases were complex systems. Would this framework also be useful for describing phases in simple systems? In a simple fluid the thermodynamic and dynamic behavior is governed by the molecular length scale. This is the case of the rare gases, diatomic and triatomic molecules. In a complex fluid, the thermodynamic and dynamic properties are governed not by the atomistic length scales but by a mesoscopic scale that arises from the competition of the multi-scale molecular forces. These systems include colloidal suspensions, gels and polymer blends. Due to the complexity of the competition forces, complex fluids can be considered homogeneous at the macroscopic scale, but are disordered at the microscopic scale, and possess structure at an intermediate scale. This is the reason why the multi-fractal spectrum employed to analyze the structural transformation by mechanical perturbations can be applied in those complex fluids as well.

Water, even though a very simple triatomic molecule, is not a simple liquid. It is an anomalous material showing a number of thermodynamic and dynamic anomalies [25]. The most familiar anomaly is its increasing density with temperature, at ambient pressure, up to 4 °C. Above this temperature water behaves as a normal liquid and density decreases as temperature rises. Experiments for water allow to locate the line of temperatures of maximum density (TMD) in the pressure–temperature plane. Below TMD, density decreases with decreasing temperature, differently from the behavior of the majority of fluids, for which density increases on lowering temperature [26].

In addition to the thermodynamic and dynamic anomalies, water exhibits many solid phases. Several coexistence lines separate the multiple solid phases. Thus, the energy landscape associated to the crystalline phases presents a number of sharp valleys with very low energies. The temperature and pressure ranges at which each one of these sharp valleys displays lowest energy values define the stable phase in that region of the phase diagram. Those valleys of the energy landscape that never achieve the lowest energy correspond to the amorphous configurations. When confined within plates, the fluid energy landscape becomes even more complex. The anomalous fluid forms layers and the system shows a transition from three layers to a two layers structure [27–29]. Using nanotubes, the same transition appears and it is associated with a dynamic transition from a normal to super-flow regime [30–33]. At low temperatures and high degree of confinement the contact layers melt, while the central layer stays liquid. The contact layer form a variety of liquid, liquid crystal and solid structures [34].

Recently a model for describing the anomalous behavior of water were studied under confinement [27]. These studies indicate that the confined system exhibits at the wall two dimensional phases not present in the bulk system [28,34–37]. While the existence of the phases is identified clearly by the instabilities of the density versus pressure phase diagram, the nature of the new structures, tested with the radial distribution function [27] and with the translational order parameter [28,34–37], it is still unclear. Particularly the system presents phases that change continuously to very different structures without phase transition while other phases change through a first order transition. These two scenarios cannot be identified by the translational order parameter analysis and need further understanding.

In this work we explore the idea that the fractal analysis can provide information of the structure and phase behavior of anomalous fluids, like water. In this context we study the phase behavior of a water-like model confined within plates. The pressure versus temperature phase diagram, of this fluid is analyzed in the framework of the multi-fractal spectrum and within this framework the different phases are identified.

The paper is organized as follows: in Section 2, the model is introduced; in Section 3, the methods are presented; the results are given in Section 4 and our final conclusions are presented in Section 5.

2. The model

The water-like fluid is composed by N spherical particles of effective diameter σ that interact through a core-softened potential of two length scales, namely

$$\frac{U(r_{ij})}{\epsilon} = 4\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right] + a\exp\left[-\frac{1}{c_0^2}\left(\frac{r_{ij}-r_0}{\sigma}\right)^2\right] \tag{1}$$

where $r_{ij} = |\vec{r}_i - \vec{r}_j|$ is the distance between two fluid particles i and j. The first term is a standard 12-6 Lennard-Jones (LJ) potential [38] and the second one is a Gaussian well centered at r_0, with depth a and width c_0. The parameters used in this work are $a = 5.0$, $c_0 = 1.0$ and $r_0/\sigma = 0.7$, that result in a potential with two length scales, one around $r_{ij} \equiv r_1 \approx 1.2\sigma$ and