

The Interpretation of Water Anomalies in Terms of Core-Softened Models

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In the first part of this paper I review the understanding of anomalous properties of water in terms of particles interacting by core-softened potentials. I discuss the origin of the bulk anomalies in terms of the two different configurations of neighbor particles: low energy–high volume and high energy–low volume. In the second part I study some anomalies of water under strong spatial confinement, namely when it lubricates a contact between two solid surfaces. Solvation and friction forces are studied as a function of lubricant thickness. Whereas for hard core particles maxima in the solvation force are correlated with maxima in the friction force, for soft core particles and appropriately chosen parameters the opposite is true. This leads to a reduction of the friction coefficient of about one order of magnitude in the second case. I argue that materials that expand when freeze may be modeled in terms of soft core particles, and that these materials are naturally good boundary lubricants.

1 Introduction

There is no doubt that water is (from many points of view) the most important liquid on earth. It cannot be denied also that it is a liquid with many anomalous properties. In searching for the origin of these anomalies, a natural question is whether they are independent of each other, or they can be ascribed to some common and fundamental origin, and if the second is the correct view (as I will argue to be the case), what this fundamental origin is. Trying to systematize the anomalous properties of water under a unifying principle, it is illuminating the observation that most of the anomalies can be re-obtained with a model of classical particles interacting with a particularly chosen spherically symmetric potential of the core-softened type. This model is simple enough as to permit a qualitative discussion of the origin of the anomalies, and the identification of its ultimate physical origin.

Core-softened potentials were first considered by Stell and Hemmer[1] some thirty years ago. However, it has been recognized only recently that these models reproduce most of the anomalous properties found in water. My presentation has the following scheme. In the first part I will briefly review results obtained in the last few years on the anomalous properties of core-softened models, in particular referring to the description of water anomalies. Hoping that this will persuade the reader that these models capture the main physics behind water anomalies, in the second part I will present results on the fluidity and lubrication properties of these models under confinement. They permit to understand why the lubricating properties of water are anomalous and also provide some ideas for the search of materials with good lubricating properties.

2 The explanation of bulk water anomalies in terms of core-softened potentials

2.1 Motivation of core-softened models. Anomalous melting and density anomaly

Although it is the nature of the hydrogen bond that gives water most of its especial character, it is more important from our point of view the statement that water is a *tetrahedral liquid*. In fact, the oxygen in the water molecule tends to form a tetrahedron with its two own hydrogens and with two other hydrogens of neighbor molecules via hydrogen bonds. The tetrahedral structure is then supported by hydrogen bonds, but from our perspective we take the tetrahedral structure as more fundamental. In fact, most of the description of anomalous properties that will be made here apply also to the whole family of *tetrahedrally coordinated materials*[2, 3]. In addition to water they include a lot of substances based on the prototypical tetrahedral (sp^3 -coordinated) elements: carbon, silicon and germanium.

In order to motivate the introduction of core-softened models, let us take a simple minded view to the anomalous melting of water. Normal ice (ice-Ih) is an open tetrahedral structure of the wurtzite type[4]. It is stable because it optimizes the potential energy of the system. Water has a higher density because water molecules can tangle in a way that is not permitted in the solid. Of course some energy has to be paid in this more compact structure, but temperature is able to provide it. We can then qualitatively say that there are two typical arrangements of water molecules[3]: low energy-high volume configurations (as realized in ice-Ih) and high energy-low volume configurations. They are

pictorially displayed in Fig. 1(a). We may wonder whether the existence of these two kinds of configurations is enough to produce the melting anomaly and also what is the simplest model we can imagine with these two configurations. The answer to the first question is positive. To address the second we introduce the core-softened Stell-Hemmer potentials.

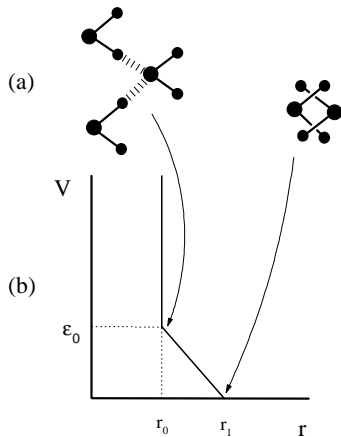


Figure 1. (a) Two types of local arrangement between water molecules: low energy–high volume (left) and high energy–low volume (right) (continuous line indicate intramolecular bonds, dashed lines are hydrogen bonds). (b) A spherically symmetric core-softened potential, with the two distances mimicking the configurations in (a).

In this model, the energy between two spherical particles in the system is composed of a hard core at some distance r_0 plus a shoulder that extends up to some other distance r_1 (see Fig. 1(b)). By now we take the potential to be purely repulsive. Some details of the potential are not relevant for the discussion. For instance, some people have studied it using a square shoulder instead of a linear one, and we will also present results for a smoothed version of the linear shoulder case. However, the crucial point is that there should be an abrupt transition between low energy–high volume configurations (represented by particles at relative distance r_1) and high energy–low volume configurations (represented by particles at relative distance r_0). Simulating a classical model of particles interacting with this potential we do observe anomalous melting[5]. In Fig. 2(a) we see the evolution of specific volume as a function of temperature for a system at pressure $P = 1.0\varepsilon_0/r_0^2$ (for clarity I show here results for a two-dimensional system). The melting transition with density increase is clearly visible. Snapshots of the system [Fig. 2(b)] show in fact that the crystalline phase is a triangular structure with lattice parameter $a \sim r_1$. In the liquid phase, however, there is energy available for neighbor particles to surmount the energy shoulder of its neighbors, and this produces a density increase upon melting. Density continues to increase after melting for a while, and then decreases starting $T \simeq 0.15\varepsilon_0$. Then this temperature marks a point of *maximum density* in the fluid, very much as real water at 4C.

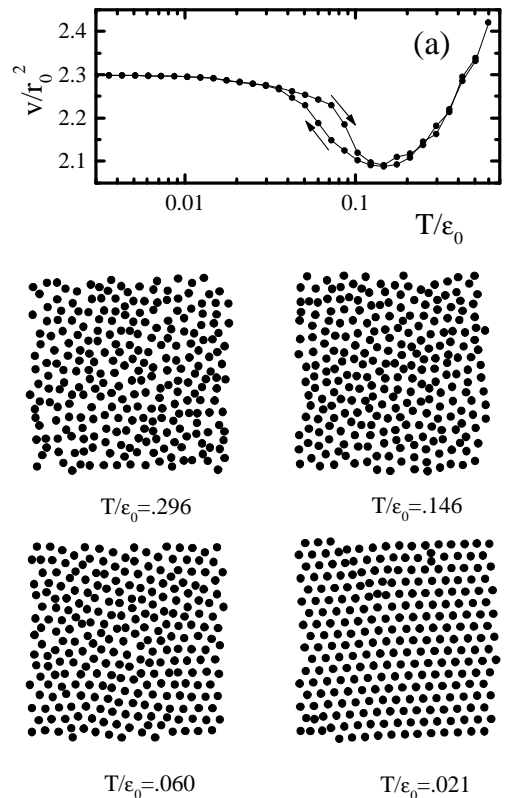


Figure 2. (a) Evolution of specific volume as a function of temperature for a two dimensional system with $r_1/r_0 = 1.65$, at pressure $P = 1.0\varepsilon_0/r_0^2$. Results were obtained decreasing and increasing temperature, as indicated by the arrows. The anomalous melting and the temperature of maximum density (minimum v) are clearly observable. (b) Snapshots of the system at different temperatures (dots indicate the hard core radius r_0 of the particles). Note that there are essentially no particles (except a few defects) at distance r_0 in the lowest temperature picture, whereas in the fluid phase, at larger temperature, there are many. This effect produces the anomalous melting and the density anomaly (adapted from Ref. [5]).

2.2 Compressibility anomaly and the second critical point

In an attempt to systematize the anomalous properties of water, H. E. Stanley and co-workers introduced[6] the hypothesis of a second critical point (SCP) in its phase diagram. The SCP would be the end point of a line of first order transition between two different liquid (or glassy, as temperature is very low) phases, very much like the normal critical point is the end point of the liquid-gas coexistence line. Estimations[6, 3] indicated that the SCP would be located in a region of the phase diagram not directly accessible, as liquid water cannot be avoided to crystallize there. However, it was Stanley's suggestion that the existence of the SCP can generate anomalies in the properties of water, even relatively far away from the critical point itself. Then the effects of the SCP are observable even if the SCP itself remains hidden.

Our studies of core-softened models[5, 7, 8, 9] (in addition to others [10, 11, 12]) allowed us to suggest a slightly

different interpretation of the relation between the SCP and thermodynamic anomalies. In my view it is not the existence of the SCP that generates the thermodynamic anomalies, but it is in some sense the opposite. To understand this let us first discuss the compressibility anomaly in core-softened models[7]. We will need to consider the supercooled liquid regime[13]. In order to study supercooled fluid phases theoretically, some mechanism has to be postulated to avoid crystallization of the system. A simple possibility is to consider a polydisperse system, formed by particles of different sizes. This may avoid crystallization, and then the fluid phase can be claimed to exist down to zero temperature (note that experimentally the system can be supercooled only in particular conditions, since the most stable configuration at low enough temperatures is ultimately a crystalline one).

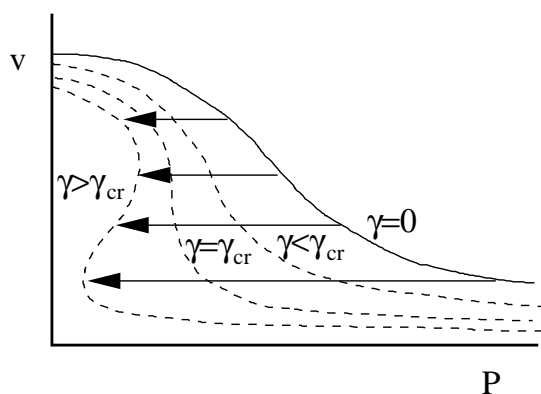


Figure 3. Qualitative evolution of specific volume vs. pressure of a core-softened model without attractive term in the supercooled regime (continuous curve). The effect of the inclusion of an attraction between particles in the van der Waals limit (i.e., replacing P by $P + \gamma/v^2$) can be seen as dashed lines for progressively larger values of γ , from right to left. In the last case a first order transition has appeared.

Let us imagine our core-softened model in the limit $T \rightarrow 0$ and without the possibility to crystallize. I will concentrate on its density vs. pressure characteristic. At very low pressures the particles behave as hard spheres of radius r_0 , since then cannot surmount the energy shoulder of its neighbors. On the other hand, at very high pressure the system behaves as a hard sphere system but now with radius r_1 , since the energy shoulder is negligible in this limit. Then we expect an evolution of specific volume (inverse of density) vs. pressure as depicted in Fig. 3 (continuous line). The transition between the low- P and high- P configurations is not expected to be sharp, since as the system is amorphous not all the particles collapse onto their neighbors at the same value of pressure. This kind of curve is in fact reproduced in simulations of the model[7, 9], as we see in Fig. 4. The compressibility coefficient is defined as $-\frac{1}{v} \frac{\partial v}{\partial P}$. It is clear that a density-pressure curve as that of Fig. 4 implies a maximum in the compressibility at some pressure, which is named the compressibility anomaly.

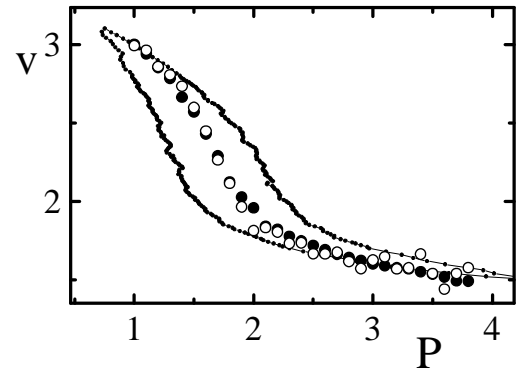


Figure 4. Results of simulations in a bidisperse system (see Ref. [9] for details) for the specific volume as a function of pressure at $T = 0$. Small dots: results from a single run increasing and decreasing pressure. Large full dots: individual simulations quenching a high temperature fluid phase down to zero temperature. Large open dots: calculated by evaluating the enthalpy h in the individual quenching runs, and then using the thermodynamic relation $v = \partial h / \partial P$, valid at $T = 0$. The almost coincidence between open and full dots indicates thermodynamic consistency. v and P are in units of r_0^2 and ε_0/r_0^2 respectively (from Ref. [9]).

The compressibility anomaly is the germ of the SCP, that appears in the model only when an attractive term of sufficient strength is included in the potential energy between particles. We can see this in the simplest case, namely, when the attractive energy is supposed to be of long range, and then treatable in the van der Waals approximation[7]. In this limit, the inclusion of an attraction between particles is equivalent to the application of a fictitious negative pressure P^{vdW} , given by $P^{vdW} = -\gamma/v^2$, where v is the specific volume of the system. The results for a system with a finite γ can then be obtained from those with $\gamma = 0$ by the substitution $P \rightarrow P + P^{vdW}$. As P^{vdW} depends itself on density, this substitution is self-consistent, and can produce non-trivial results. We can see in Fig. 3 the qualitative effect of this substitution on the original (continuous) curve. If γ is larger than some critical value γ_{cr} , the density-pressure curve becomes reentrant, and this implies a first order transition between two fluid phases (Fig. 5). Then, it is the compressibility anomaly together with an attractive part in the interaction that generate the SCP in core-softened models. The ability of these models to reproduce the anomalies in water suggests that this qualitative explanation applies also to real water, and then that the SCP is a consequence of the compressibility anomaly, and not the opposite. As an additional evidence supporting this view, I note that the SCP seems to exist in water [14], but it does not seem to occur in some other tetrahedral materials that share many of the anomalies of water. This may be the situation in silica, for instance[9, 15, 16].

2.3 Other bulk anomalies

Other anomalies found in water are also observed in core-softened models. Water is characterized by many different crystalline phases[4]. It is remarkable that the very simple,

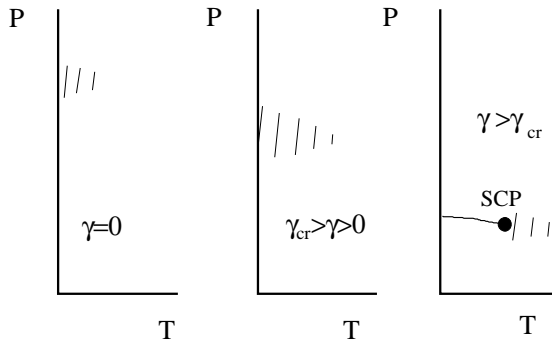


Figure 5. The supercooled pressure-temperature phase diagram of core-softened potentials as a function of the intensity γ of the van der Waals attraction. The dashed region indicates the zone of the compressibility anomaly. If the attraction is larger than some value γ_{cr} , the compressibility anomaly generates a first order transition line and the SCP appears (the normal liquid-gas critical point is not indicated).

spherically symmetric core-softened model we are studying has also different crystalline structures. In two dimensions, in addition to the triangular one, the structures shown in Fig. 6 are stable in different regions of the P - T plane[5]. Even a quasi-crystalline phase becomes stable in a region of parameters[5]. In three dimensions the possible crystalline structures have not been surveyed in detail, but it seems in fact that there are many[17].

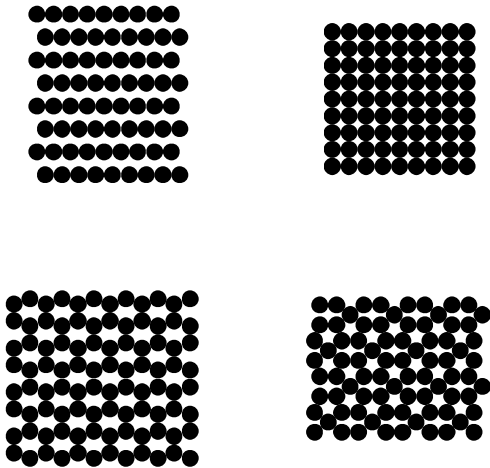


Figure 6. Other crystalline configurations for the two dimensional system, stable under particular pressure-temperature conditions (see Ref. [5] for details).

The last anomaly I will mention is of dynamic nature. It concerns the diffusivity of single particles in thermal equilibrium. In most liquids, this quantity is a monotonically decreasing function of pressure, as pressure constraints the movement of particles by caging them more tightly by its neighbors. In water, diffusivity first *increases* as a function of pressure, reaches a maximum and then decreases[18]. The increasing diffusivity with pressure is observed in core softened models[19, 12]: at low pressures particles do not have the possibility of going onto the energy shoulders of their neighbors. As pressure increases these states become

accessible as intermediate steps in the process of diffusion of single particles, and an increase of diffusivity is observed.

3 Lubricity and fluidity under confinement

Among the many anomalous properties of water there is its tendency to remain fluid even when strongly confined spatially[20, 21]. This property is puzzling since water molecule is rather spherical, and it is known that for most liquids with more or less spherical molecules, confinement produces a tendency to solidify[22, 23, 24], and in the end, a strong reduction in diffusivity. Actually it is this confinement-induced solidification one of the most serious problems when using fluid lubricants in the so-called boundary regime[24], in which only few molecular layers of lubricant remain between the lubricate solids. In these nanocontacts, the hydrodynamic lubrication regime[24] breaks down, and most of the friction and wear between the two surfaces originates there. This problem would be severe in the operations of micro-electromechanical machines (MEMS), which up to now are usually used unlubricated.

Careful measurements using water films down to one or two molecular layers indicate that water performs extremely well as lubricant in this regime[20], which is again an indication of its high lubricity under strong confinement. Understanding these anomalous properties of water in the simplest way may contribute with some new ideas in the design of new lubricants for miniaturized equipment. I will present here some qualitative considerations of how the lubricity of water is preserved under strong confinement. The analysis will be based –again– in the use of core-softened models to qualitatively mimic the behavior of water[25].

If we squeeze a liquid film between two solid contacts, the liquid opposes a force, which is known as the solvation force[23, 24]. When studying the solvation force at nanocontacts, oscillations as a function of the distance between solids are usually observed. Maxima of the solvation force correspond to well structured, quasi-solid lubrication films, and then to maxima in the friction force when the surfaces are sheared. Minima of the solvation force correspond in turn to a lubricant film that is more fluid-like, and then to minima in the friction force. This is qualitatively depicted in Fig. 7. The transition between a maximum and a minimum of the solvation force upon reduction of the distance corresponds to the squeezing of a full layer of lubricant out of the contact. In experiments, a condition of constant load on the contact is usually realized (this load being typically the yield stress of the softer material), instead of a constant distance situation. Then the ranges of distances corresponding to low friction forces (which correspond to a *negative* solvation force with respect to the bulk pressure in the lubricant) are not accessible in standard experiments.

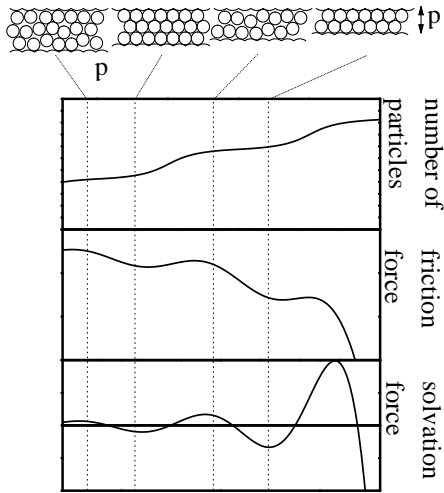


Figure 7. Qualitative evolution of the solvation and friction forces, and the number of particles in the gap as a function of the distance separating the confining walls, in a system with hard core interaction. The solvation force oscillates around the value corresponding to the bulk pressure in the lubricant. The correlation between solvation and friction forces is positive.

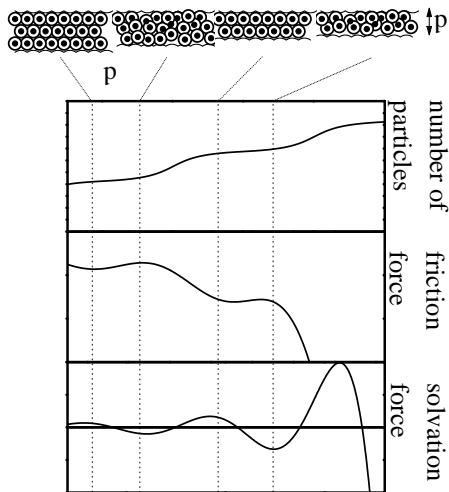


Figure 8. Same as previous figure for a system of core softened particles (the two radii of the particles are indicated in the drawings below). Now decreasing the distance between confining walls may cause the lubricant to become more fluid without squeezing out particles. This leads to a negative correlation between solvation and friction forces.

The situation can be thought to be different for core softened-particles, as depicted in Fig. 8. Now a reduction of the distance between the solids can be thought to produce a disordering of the lubricant particles *without* implying the squeezing out of them. This means for instance that under

the transition between the two right-most configurations in Fig. 8, the solvation force increases (since we are compressing a system with a fixed number of particles) but friction force decreases (since the system becomes more fluid). This leads to an overall negative correlation between solvation force and friction force. Since (as already said) typically only the upper parts of the oscillation of the solvation force are accessible experimentally, this implies that the minimum friction force is accessible, and this is experimentally desirable.

Results of molecular dynamics simulations with core-softened models support this qualitative description. I refer to Ref. [25] for details of the simulations. In Figs. 9 and 10 we see the results of simulations in two different cases. In Fig. 9 the externally applied pressure is such that the lubricating fluid behaves essentially as a hard core system (point A in [25]). We see the positive correlation between solvation (F_s) and friction (F_f) forces, as in the qualitative description of Fig. 7. In 10, instead, the pressure is such that the fluid behaves anomalously (point B in [25]). Now the correlation between F_s and F_f is negative. Due to this, the friction coefficient attained (calculated in a standard way as $F_f/(F_s - F_0)$, F_0 being the reference force due to the bulk pressure in the lubricant) is about one order of magnitude lower.

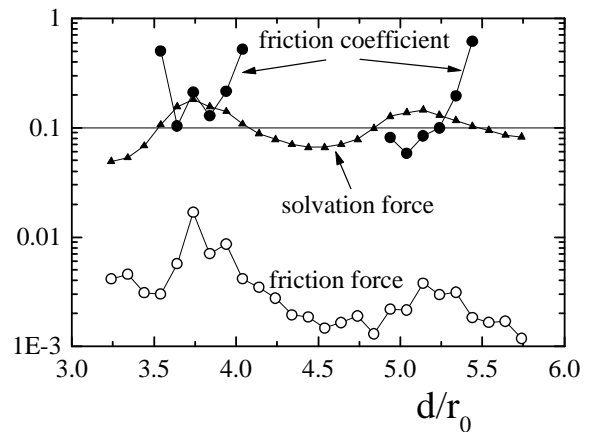


Figure 9. Results of numerical simulations in a 'normal' point of the phase diagram, in which particles behave essentially as hard core particles (point 'A' in Ref. [25]. See it for details). Friction F_f and solvation F_s forces (per unit area) are in units of ϵ_0/r_0^3 . F_f is calculated by keeping the distance d as fixed, at a shear velocity given by $v = 10^{-2}v_0$, with $v_0 = \sqrt{\epsilon_0/m}$, m being the mass of the particles. Note that F_s oscillates around $F_0 = 0.1\epsilon_0/r_0^3$, which is the value corresponding to the bulk pressure of the lubricant. There is a positive correlation between F_f and F_s , as in the qualitative description of Fig. 7. d measures the distance between the planes containing the center of the particles in the walls. Within those plains particles are accommodated in a rigid triangular lattice, as explained in Ref. [25].

We may also approach with this model the issue of high lubricity of water in nanocontacts[21] (something of course closely related to its lubricating properties). I will present results from molecular dynamics for the diffusivity of particles forming a mono-layer between two solid surfaces, again in points A (normal) and B (anomalous) of the phase diagram.

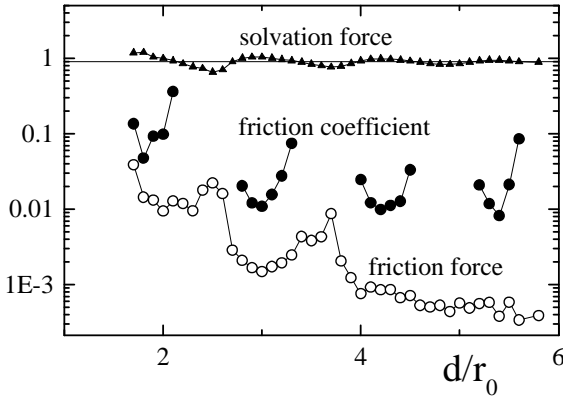


Figure 10. Same as previous figure, now in an ‘anomalous’ point of the phase diagram (point ‘B’ in Ref. [25]). F_f is calculated at a shear velocity of $v = 5 \times 10^{-3} v_0$. The correlation between F_f and F_s is now negative, as in the qualitative description of Fig. 8. Note that the range of friction coefficients that are obtained in this case is about one order of magnitude lower than in the previous figure.

Diffusivity D is numerically calculated from the time evolution of the position of a single particle during the molecular dynamics simulation as

$$|\mathbf{r}(t) - \mathbf{r}(0)|^2 = 2D\delta t, \quad (1)$$

where δ is the dimensionality of the system. Results are shown in Fig. 11 for three different configurations of the confining walls: (i) crystalline commensurate (in which walls consist of fixed particles on a triangular lattice, with lattice parameter equal to the equilibrium bulk lattice parameter at the corresponding pressure, and the top and bottom walls are in register); (ii) crystalline rotated (same as before, but top and bottom walls rotated relatively 26 degrees around the normal); (iii) disordered (walls formed by particles located at random, with the maximum density possible under the restriction that no particles in the walls are closer than $0.8 r_1$ from each other). We also see in Fig. 11 the bulk diffusivity of particles in three dimensions at the same conditions. The general trend is that diffusivity decreases when temperature is reduced. In the normal case however, this decrease is much more rapid than in the anomalous case, and at the melting point, the diffusivity of confined particles in the normal regime is about a factor of 20 lower than in the anomalous case, comparing equivalent configurations of the confining walls. Then it can be concluded that confinement has an effect more drastic on the diffusivity of particles interacting through hard core interactions. For particles interacting through interactions of the core-softened type, the effect of confinement is much lower. A qualitative explanation can be given. In the strongly confined regime, the corrugation of the potential generated by the walls is an important factor affecting the mobility of particles. Strong corrugation is typically related with low mobility. Hard core interactions produce a strongly corrugated potential. For the core-softened interaction instead, there is a range of distances on which the corrugation potential becomes anomalously small (see Fig.

12). If the external pressure is such that particles of the film locates close to this distance from the wall, the confinement effect of the walls is reduced, favoring a greater diffusivity of the particles. This idea may serve as a starting point for the design of lubricants based on tetrahedrally coordinated materials.

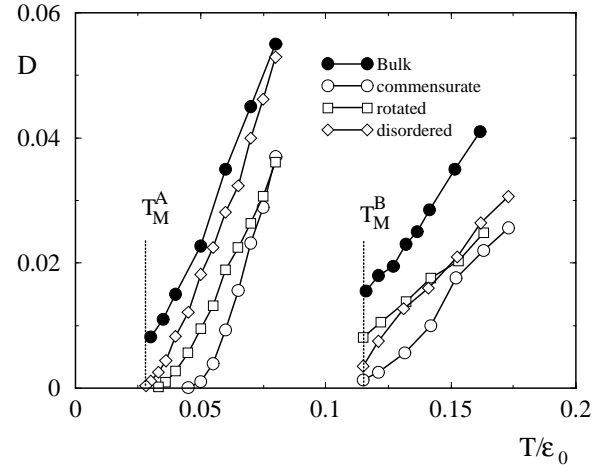


Figure 11. Diffusivity of particles forming a single layer between two confining hard walls, in the normal (point A, $P = 0.1\epsilon_0/r_0^3$, left curves) and anomalous (point B, $P = 0.9\epsilon_0/r_0^3$, right curves) case (see Ref. [25]), as a function of temperature. The bulk melting temperature in both cases is indicated. Calculations were done with a solvation force per unit area of ten percent of the bulk pressure. D is in units of $r_0\sqrt{m/\epsilon_0}$. Three different cases are considered for the arrangement of particles in the confining walls (see text): (i) crystalline commensurate, (ii) crystalline rotated, and (iii) disordered.

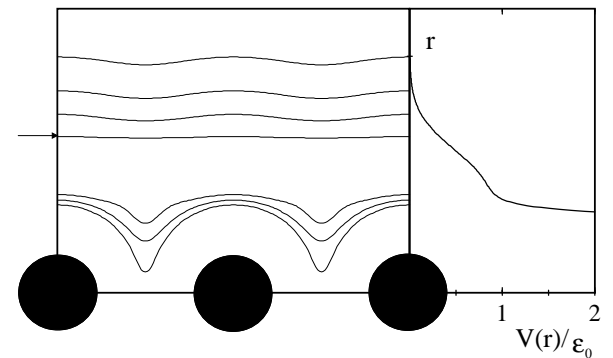


Figure 12. One dimensional example of the corrugation potential. Lines of equal vertical force for a probe particle interacting with particles aligned on a straight line with the potential indicated at the right. The maximum slope of these lines is the static friction coefficient for the probe particle. Note that there is an intermediate distance (roughly indicated by the arrow) in which the corrugation potential is particularly low.

4 Conclusions

I have tried to present in this work my understanding of the anomalous properties of water and tetrahedrally coordinated

materials obtained from studies of core-softened model potentials. It seems to me that these models capture the main physics behind the anomalies, and this is the existence of two different kinds of local arrangement of particles, with an abrupt transition between the two. Although quantitative predictions for water or other specific materials are not expected to be obtainable from the core-softened calculations (at least in the present form), they provide a simple, yet qualitatively comprehensive framework that is useful both to understand well known properties, and also to suggest unexpected behaviors.

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References

- [1] P. C. Hemmer and G. Stell, Phys. Rev. Lett. **24**, 1284 (1970); G. Stell and P. C. Hemmer, J. Chem. Phys. **56**, 4274 (1972); J.M. Kincaid, G. Stell, and E. Goldmark, J. Chem. Phys. **65**, 2172 (1976).
- [2] C. A. Angell, R. D. Bressel, M. Hemmati, E. J. Sare, and J. C. Tucker, Phys. Chem. Chem. Phys. **2**, 1559 (2000).
- [3] O. Mishima and H. E. Stanley, Nature (London) **396**, 329 (1998).
- [4] P. V. Hobbs, *Ice Physics*, Clarendon Press, Oxford, 1974; V. F. Petrenko and R. W. Withworth, *Physics of ice*, Oxford University Press, Oxford, 1999.
- [5] E. A. Jagla, Phys. Rev. E **58**, 1478 (1998).
- [6] P. H. Poole, F. Sciortino, U. Essmann, and H. E. Stanley, Nature (London) **360**, 324 (1992).
- [7] E. A. Jagla, J. Chem. Phys. **111**, 8980 (1999).
- [8] E. A. Jagla, Phys. Rev. E **63**, 061501 (2001).
- [9] E. A. Jagla, Phys. Rev. E **63**, 061509 (2001).
- [10] G. Franzese, G. Malescio, A. Skibinsky, S. V. Buldyrev, and H. E. Stanley, Nature (London) **409**, 692 (2001).
- [11] M. R. Sadr-Lahijany, A. Scala, S. V. Buldyrev, and H. E. Stanley, Phys. Rev. Lett. **81**, 4895 (1998).
- [12] A. Scala, M. R. Sadr-Lahijany, N. Giovambattista, S. V. Buldyrev, and H. E. Stanley, Phys. Rev. E **63**, 041202 (2001)
- [13] P. G. Debenedetti, *Metastable Liquids*, Princeton University Press, Princeton, 1997.
- [14] O. Mishima, L. D. Calvert, and E. Whalley, Nature (London) **310**, 393 (1984); **314**, 76 (1995); O. Mishima, K. Takemura, and K. Aoki, Science **254**, 406 (1991); O. Mishima, J. Chem. Phys. **100**, 5910 (1994).
- [15] D. J. Lacks, Phys. Rev. Lett. **84**, 4629 (2000); E. A. Jagla, Phys. Rev. Lett. **86**, 3206 (2001); D. J. Lacks, Phys. Rev. Lett. **86**, 3207 (2001);
- [16] K. Trachenko and M. Dove, Phys. Rev. B **67**, 064107 (2003).
- [17] E. A. Jagla, J. Chem. Phys. **110**, 451 (1999).
- [18] F. X. Prielmeier, E. W. Lang, R. J. Speedy, and H. -D. Lude-mann, Phys. Rev. Lett. **59**, 1128 (1987).
- [19] E. A. Jagla, Mol. Phys. **99**, 753 (2001).
- [20] A. M. Homola, J. N. Israelachvili, M. L. Gee, and P. M. McGuiggan, J. Tribology **111**, 675 (1989); J. N. Israelachvili, Surf. Sci. Rep. **14**, 109 (1992).
- [21] U. Raviv, P. Laurat, and J. Klein, Nature (London) **413**, 51 (2001).
- [22] C. Rhykerd, M. Schoen, D. Diester, and J. Cushman, Nature (London) **330**, 461, (1989); P. A. Thompson and M. O. Robbins, Science **250**, 792 (1990).
- [23] B. Brushan, J. N. Israelachvili, and U. Landman, Nature (London) **374**, 607 (1995).
- [24] B. N. J. Persson, *Sliding Friction: Physical Principles and Applications*, Springer, Heidelberg, 1998.
- [25] E. A. Jagla, Phys. Rev. Lett. **88**, 245504 (2002).