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Applications of the Stell–Hemmer Potential to Understanding Second Critical Points in Real Systems

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We consider the novel properties of the Stell–Hemmer core-softened potentials. First we explore how the theoretically predicted second critical point for these potentials is related to the occurrence of the experimentally observed solid–solid isostructural critical point. We then discuss how this class of potentials can generate anomalies analogous to those found experimentally in liquid water.

KEY WORDS: Simple liquids; core-softened potentials; liquid–liquid critical point; density anomaly; diffusivity anomaly; liquid water; liquid metals.

Simple liquids are often modeled by pairwise potentials possessing a repulsive core, mimicking the impenetrability of atoms or molecules, and an attractive part, responsible for the gas–liquid transition. For a fluid in which the interaction potential $\phi(r)$ has a hard core plus an attractive part, a "softened" hard core (Fig. 1) can produce an additional line of phase transitions.(1) A general argument by Stell and Hemmer based on the symmetry between occupied and unoccupied cells in lattice gas models of fluids predicts that the additional line of phase transitions can end at a novel critical point.(1, 2) An explicit example of the occurrence of a second line of first order transitions is given in ref. 1 for a one-dimensional continuum model of a fluid with long-range attraction;(3) this first order line can end in a critical point depending on the details of the core-softened potential. The general result is that if the repulsive part (core) of the interaction potential has a concave part (which makes it "core-softened"), then it is likely that such a novel transition occurs.(4) Stell and Hemmer(1) relate the occurrence

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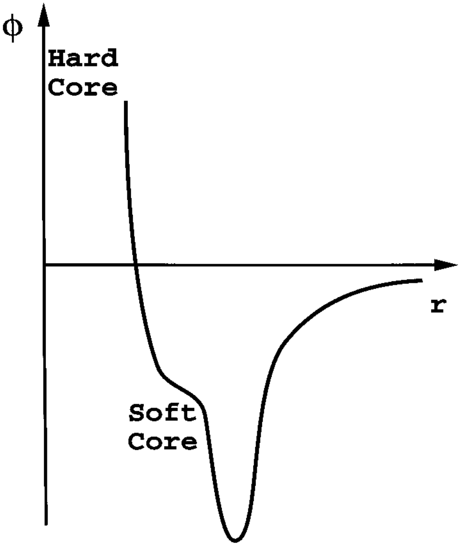

Fig. 1. Example of core-softened potential (the soft core is a region where the potential is concave).

of a high-density, low-temperature critical point to the known isostructural solid–solid critical point observed in some experiments.(5)

To understand the occurrence of a second transition, consider the Gibbs potential at zero temperature. The shape of the energy U as a fuction of the volume V should have the same "core-softened" shape (i.e., possesses a region where it is concave) as the inter-particle potential. The stable phase is then determined by the Gibbs potential

$$G(P, T) \equiv \min_V \{ U + PV - TS \} \tag{1}$$

where S is the entropy. The right hand side of (1) is shown in Fig. 2 as a function of V, for $T = 0$ and for different values of pressure P. At low P, the stable phase of the system has a specific volume at which the average inter-particle distance is near to the minimum of the inter-particle potential. The concavity in U assures that, on increasing P, an additional minimum appears in $U + PV - TS$. For high enough P, this minimum will become the lowest one and the stable phase of the system will be the one for which the mean inter-particle distance is "inside" the softened part of the core.

For one-dimensional models, a first-order transition at $T = 0$ between a dense and an open phase occurs at a pressure that can be determined exactly with the graphical construction of Fig. 2.(6, 7)

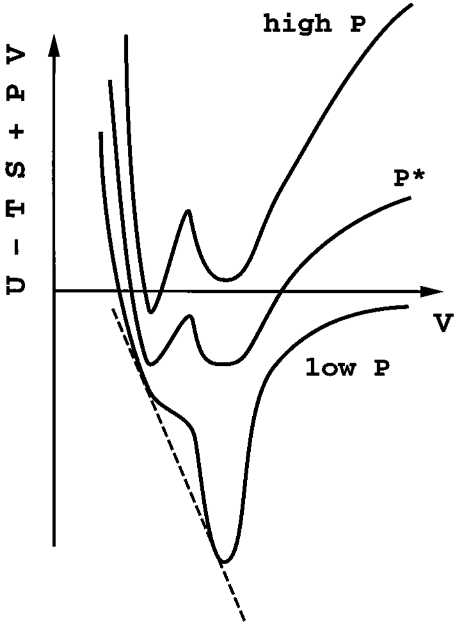

Fig. 2. The shape of $U+PV-TS$ at $T=0$ for various P. Note the evolution of the minima with pressures: at high enough pressure the absolute minimum is at higher densities than the absolute minimum at low pressures, signaling a first order transition. The transition occurs at the pressure P^* equal to the absolute value of the slope of the long-dashed line, representing the tangent to $U+PV-TS$ for $T=0$, $P=0$. By geometrical construction, $U+PV-TS$ has a horizontal tangent between two minima of equal depth at $T=0$, $P=P^*$.

For short-range interactions, the entropy gives a huge contribution in one dimension, making any phase transition disappear for $T>0$. Hence, the contribution of the entropic term TS makes the double well structure of Fig. 2 disappear when $T>0$. This may not be true in higher dimensions, and so a line of first order transitions (eventually ending in a critical point) could be present for $T>0$.

Stronger evidence for the occurrence of a high-density, low-temperature critical point is given in ref. 8 upon developing and refining analytic methods to investigate the high-density region of the phase diagram of a fluid. The methods used are in principle for a dense fluid, and hence would predict a liquid–liquid transition. However, the second critical point can be related to the isostructural critical point occurring in the solid phase of materials such as Cs, Ce and of mixtures such as Sm-S and Ce-Th.(9) For all these materials the shape of the effective pair potential is "core-softened."(10)

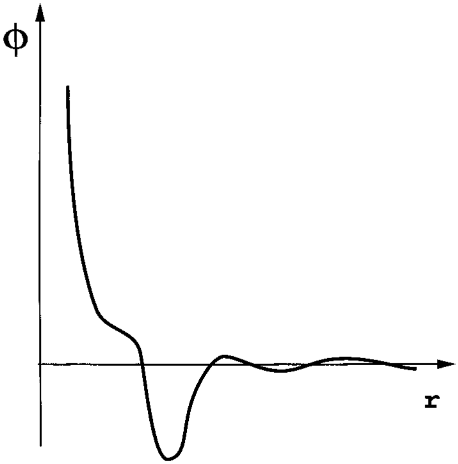

Fig. 3. Schematic form of the potential as obtained from the inversion of scattering data or from first principle calculations. See, e.g., refs. [12] and [16].

Many liquid metals (Ga and Sn are prominent examples) have static structure factors $\mathcal{S}(k)$ that show weak subsidiary maxima, or asymmetries, in the main peak of $\mathcal{S}(k)$ that suggest the presence of a "structured" core that is not infinitely steep. First-principle calculation of the effective ion–ion potential for Ga leads to a core-softened potential.(11) Mone Carlo simulations with this potential reproduce for Ga the observed anomalies in $\mathcal{S}(k)$. In this case, the core-softening is not related to the oscillations seen in the tails of effective ion–ion potentials for liquid metals, but arises from the fluctuations in polarizability of the nuclues; hence, core-softening can be expected for highly polarizable ions. Inversion of the experimental structure factors for In, Zn, Al, Ge, Sn, Cs, Rb, Tl, and Pb, using random phase approximation or the Ornstein–Zernike equation with a closure, also results in effective core-softened potentials (Fig. 3).(12)

In addition to the second critical point, core-softened potentials can produce a density anomaly, i.e., the material can expand upon cooling. The occurrence of crossing isotherms was observed in the model.(13) It was noted that, although isotherms crossing is not a common feature in fluids, it is to be found whenever $(\partial V/\partial T)_P$ changes sign, as it does in water at approximately 4°C and atmospheric pressure. Using thermodynamic arguments, Debenedetti *et al.* also noted that a "softened core" can cause the thermal expansion coefficient $\alpha_P \equiv (1/V)(\partial V/\partial T)_P$ to be negative.(14)

One-dimensional fluids(15) with core-softened potentials have been studied in relation to the molecular origin of the negative thermal expansion in two fluids, water and tellurium,(6) which have an effective core-softened potential.(12, 16)

Conversely, various lines of reasoning led to the introduction of phenomenological potentials for water that are core-softened.(17) Although the hydrogen bond is highly directional so that an anisotropic potential is needed in order to reproduce quantitatively the behavior of water, a first approximation consists in assigning a lower energy to a state in which particles are further away from the hard-core, in order to induce a solid phase with a specific volume higher than the liquid phase, as is the case of water. The strong entropy reduction due to orientational bonding of water molecules can be mimicked having a narrow energy well corresponding to the inter-molecular distances of the "expanded" solid.

The inversion of the oxygen–oxygen radial distribution function $g_{oo}(r)$ for water gives an effective potential ϕ (Fig. 3) that is core-softened.(16) Thus core-softened potentials can be considered as zeroth-order models for water.

It is natural to expect that a core-softened potential can induce a density anomaly. In a liquid, the typical inter-particle distance is distributed inside the attractive part of the potential. As temperature decreases, the distribution peaks around the minimum of the potential, causing the system to expand (Fig. 4).

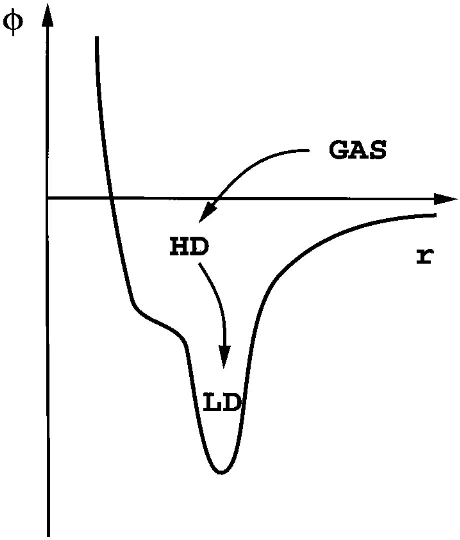

Fig. 4. On cooling from high temperatures, the system first condenses in a liquid where the typical inter-particle distance is distributed inside the attractive part of the potential. Further cooling causes the distribution to be more peaked around the minimum of the potential, making the liquid expand (HD = high density, LD = low density).

In addition to the density anomaly, further studies$^{(7)}$ of core-softened one-dimensional fluids have discovered anomalies in the isothermal compressibility and specific heat response functions in water. These anomalies are related to the existence of a critical point at $T=0$ and high density, similar to what is conjectured to occur in real water.$^{(18)}$

The region where the liquid has a density anomaly must have an upper boundary in the *P*-*T* plane; this boundary defines the line of density maxima (T_{Md}). The occurrence of this boundary can be understood by first recalling that$^{(19)}$

$$\alpha_P \propto \langle \delta V \, \delta S \rangle \propto (P\langle (\delta V)^2 + \langle \delta V \, \delta E \rangle) \tag{2}$$

When α_P is negative, the term $\langle \delta V \, \delta E \rangle$ must also be negative; the fluctuations that give a negative sign to $\langle \delta V \, \delta E \rangle$ correspond to the regions of the fluid where particles penetrate the softened part of the core. However, the α_P anomaly must vanish at high enough pressures where the positive $P\langle \delta V^2 \rangle$ term dominates.

Core-softened potentials with no attractive part and no liquid–gas transition were studied in 2 and 3 dimensions by Young and Alder, giving a *P*-*T* phase diagram with a solid–fluid coexistence line similar to Ce or Cs.$^{(20)}$ The fluid–solid coexistence line has a negatively sloped region, as in water. The phase diagram for a core-softened potential in 2d with no attractive part has been studied by Jagla,$^{(21)}$ who explicitly finds a density anomaly in the fluid region. These results indicate that the softened part of the core can be solely responsible for the density anomaly and suggest that it can be related to the existence of negatively-sloped melting lines.

The slope of a melting line is related through the Clausius–Clapeyron equation $dP/dT = \Delta S/\Delta V$ to the difference ΔS in the entropies and ΔV in the volumes between the fluid and the solid. On the other hand, the sign of the coefficient of thermal expansion $\alpha_P \propto \langle \delta S \, \delta V \rangle$ depends of the cross-correlation between entropy and volume fluctuations. Near a melting line, one expects the relevant fluctuations in a liquid to be "solid-like" as they trigger the nucleation process leading to the first order liquid–solid transition (Fig. 5). This means that the sign of $\alpha_P \propto \langle \delta V \, \delta S \rangle$ will be likely the same as $dP/dT = \Delta S/\Delta V$.

Extensive studies of core-softened potentials in two dimensions via molecular dynamics simulations$^{(7)}$ reveal a phase diagram (Fig. 6) similar to that of water (Fig. 7).$^{(22)}$ Near the negatively-sloped part of the liquid–solid freezing line ($\Delta S/\Delta V < 0$), the liquid exhibits a density anomaly ($\alpha_P \propto \langle \delta S \, \delta V \rangle < 0$). In agreement with the thermodynamic considerations of ref. 23, the model also reproduces the existence of a region where the isothermal compressibility grows anomalously upon cooling in the same

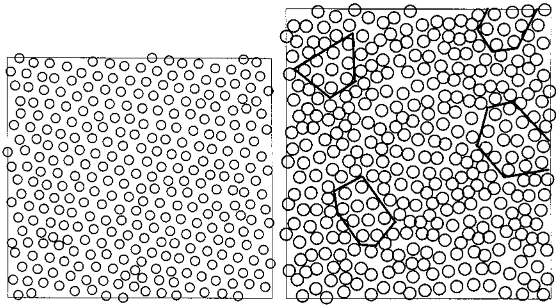

Fig. 5. Snapshot of a low density crystal (left panel) and of a liquid (right panel), both near the freezing line at low pressures, for the two-dimensional core-softened model of ref. [7]. Corresponding to the fact that the freezing line is negatively sloped, we note the appearance in the liquid of local arrangements of the particles (black "fences") resembling the low density crystal.

way as in water. Moreover, the model succeeds in reproducing anomalies not only in the statics, but also in the dynamics: there is a region in which the diffusion constant anomalously increases with pressure(7) as in water. The locus of points where the diffusivity has a maximum upon varying pressure defines the pressure of maximum diffusivity line (P_{MD}), which has been observed in water, in core-softened models, and in SPC-E simulated

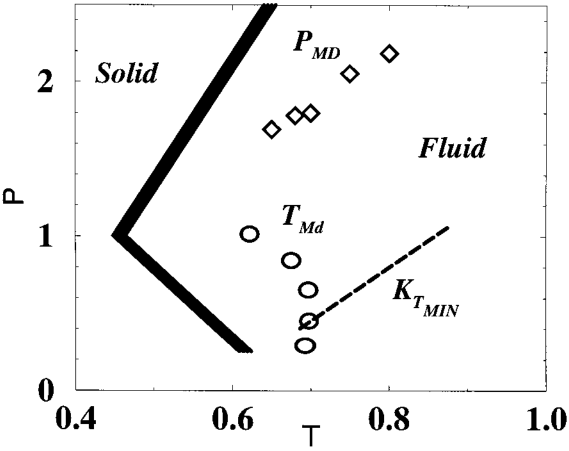

Fig. 6. Sketch of the phase diagram as found in ref. [7]. On the left of the $K_{T\min}$ line, the isothermal compressibility increases upon cooling. On the left of the T_{Md} line density decreases upon cooling. Below the P_{MD} line, diffusivity increases upon pressure. Note that the density anomaly is in the region of the liquid where the melting line is negatively sloped.

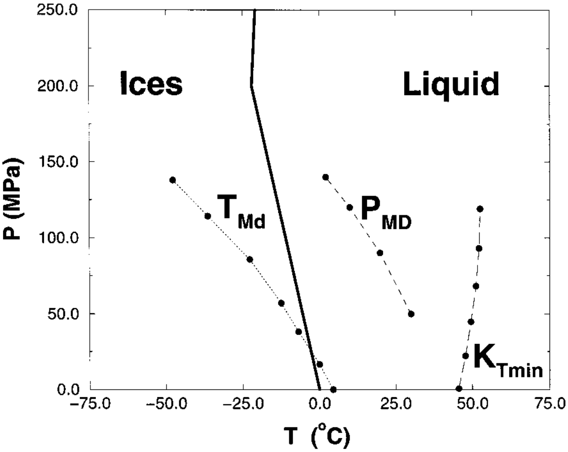

Fig. 7. Sketch of the phase diagram of water. The portions of the $K_{T\,\mathrm{min}}$, T_{Md} and P_{MD} that are beyond the melting line corresponds to experiments in the supercooled region of water. Notice that the presence of a density anomaly in the region of the negatively sloped melting line can occur in the metastable phase of the liquid. Data are obtained from ref. [22].

water;(7, 22, 24, 25) in all these cases the P_{MD} line occurs at higher pressures than the T_{Md} line. The joint occurrence of density and diffusivity anomalies is also observed in two-dimensional simulations of the Gaussian-core model(26) that, although not possessing a hard core, has a concave region in the repulsive part of the potential.

Theories relating diffusivity to entropic contributions(27) would predict the occurrence of an anomaly in the diffusion $(\partial D/\partial P)_T > 0$ to be related to an anomaly in the entropy $(\partial S/\partial P)_T > 0$. On the other hand, whenever there is a density anomaly, an entropy anomaly occurs, as the entropy reaches a maximum along isotherms on the T_{Md} line. This is a consequence of the Maxwell relation $(\partial S/\partial P)_T = -(\partial V/\partial T)_P$.

In conclusion, core-softened potentials are simple realistic potentials that can model complex fluid behavior. In addition to the well-known liquid–gas transition, an analysis of the shape of free energies at low temperatures reveals the presence of a second transition, which can either be interpreted as a solid–solid or a liquid–liquid transition. Simulations indicate that if a liquid–liquid critical point exists it is likely to be in the region of the phase diagram where the liquid is metastable, at least for core-softened potentials in two dimensions.(7) The presence of a liquid–liquid critical point provides one explanation of how anomalies in the response functions for core-softened potentials could occur—although other scenarios are also possible.(28) Although core-softened potentials are capable of exhibiting most of the anomalies present in liquid water, most materials that are known to have an effective core-softened potential have not been studied as extensively as water, and thus the presence of anomalies in them is still an open question. Moreover, the relationship between anomalies of static (e.g., entropy) and dynamic (e.g., diffusivity) quantities is still an open issue that can be explored using core-softened potentials, possibly within the framework of existing theories.(27)

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$$\alpha_P \equiv (1/\langle V\rangle)\,\partial\langle V\rangle/\partial T \propto (-\partial/\partial\beta)\langle V\rangle \tag{3}$$

and

$$(-\partial/\partial\beta)\langle V\rangle = \langle V(E+PV)\rangle - \langle V\rangle\langle E+PV\rangle = \langle \delta V\,\delta E\rangle + P\langle(\delta V)^2\rangle \tag{4}$$

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