Physics of the Liquid-Liquid Critical Point

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Within the inherent structure thermodynamic formalism introduced by Stillinger and Weber [F. H. Stillinger and T. A. Weber, Phys. Rev. A **25**, 978 (1982)], we address the basic question of the physics of the liquid-liquid transition and of density maxima observed in some complex liquids such as water by identifying, for the first time, the statistical properties of the potential energy landscape responsible for these anomalies. We also provide evidence of the connection between density anomalies and the liquid-liquid critical point. Within the simple (and physically transparent) model discussed, density anomalies do imply the existence of a liquid-liquid transition.

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Water, the most important liquid for life, belongs to a class of liquids for which the isobaric temperature dependence of the density has a maximum. In contrast with ordinary liquids, water expands on cooling below 4 °C at atmospheric pressure. This density anomaly is associated with other thermodynamic anomalies, such as minima in the compressibility along isobars and an increase of the specific heat on cooling [1]. Recent fascinating studies have attempted to connect these anomalies to the presence of two different liquid structures, separated at low temperature by a line of first-order transitions, ending in a second-order critical point [2–4]. In the case of water, this novel critical point would be located in an experimentally inaccessible region [5]. Despite this unfavorable location, the postulated presence of this critical point provides a framework for interpreting [6] not only features of the liquid state but also the phenomenon of polyamorphism and the first-order-like transition between polyamorphs [7]. In this Letter we aim at identifying the statistical properties of the potential energy landscape (PEL) responsible for the density maxima and the connection to the physics of the liquid-liquid transition.

The study of the statistical properties of the PEL—i.e., of the number, shape, and depth of the basins composing the potential energy hypersurface—is under tremendous development. Theoretical approaches, based on the seminal work of Stillinger and Weber [8], combined either with calorimetric data [9–11] or with analysis of extensive numerical simulations [12–14] are starting to provide precise estimates of the statistical properties of the PEL in several materials and models for liquids. A simple model for the statistical properties of the landscape, supported by recent numerical studies [14–16], can be built on the basis of the two following hypotheses.

(i) A Gaussian distribution for $\Omega(e_{\rm IS})de_{\rm IS}$ [15,17–20], the number of distinct basins of energy depth $e_{\rm IS}$ between $e_{\rm IS}$ and $e_{\rm IS}+de_{\rm IS}$; i.e.,

$$\Omega(e_{\rm IS})de_{\rm IS} = e^{\alpha N}\frac{e^{-(e_{\rm IS}-E_0)^2/2\sigma^2}}{\sqrt{2\pi\sigma^2}}de_{\rm IS}. \quad (1)$$

Here $e^{\alpha N}$ counts the total number of PEL basins (N being the number of molecules), E_0 is the characteristic energy scale, and σ^2 is the variance of the distribution. A Gaussian distribution is suggested by the central limit theorem, since in the absence of diverging correlation, $e_{\rm IS}$ can be written as the sum of the inherent structure (IS) energy of several independent subsystems.

(ii) A (multidimensional) parabolic shape of the PEL basins. This hypothesis is equivalent to assuming that the T dependence of basin exploration is governed by a harmonic vibrational free energy $f_{\rm vib}$. For a system of rigid water molecules

$$f_{\rm vib}(e_{\rm IS},T) = k_BT\sum_{i=1}^{6N-3}\ln[\beta\hbar\omega_i(e_{\rm IS})], \quad (2)$$

where $\hbar$ is Planck's constant, $\beta = 1/(k_BT)$ and k_B is the Boltzmann constant, and ω_i is the frequency of the ith normal mode. As suggested by numerical evidence [14–16], the relation between the parabolic basin volume and the basin depth is assumed to be linear and the linearity is quantified by two parameters a and b by writing $\sum_{i=1}^{6N-3}\ln[\omega_i(e_{\rm IS})] = a + be_{\rm IS}$. More accurate descriptions for $f_{\rm vib}(e_{\rm IS},T)$, incorporating anharmonic corrections, can be employed [21] if accuracy in the model is required. In this work, which focuses on the connection between landscape features and thermodynamic scenarios, the simple harmonic expression is considered. Accounting for anharmonic corrections does not affect the main conclusion of this work.

For this harmonic Gaussian landscape model, the three parameters α, E_0, σ^2 (modeling the statistical properties of the PEL) and the two parameters a and b(modeling the relation between basin shape and depth) fully determine the free energy of the liquid. The corresponding equation of state (EOS), expressed in terms of the V derivative of the landscape properties, is [22]

$$P(T,V) = \mathcal{P}_{\rm const} + T\mathcal{P}_T + T^{-1}\mathcal{P}_{1/T}, \quad (3)$$

where $\mathcal{P}_{\rm const}(V) = -\frac{d}{dV}[E_0 - b\sigma^2]$, $\mathcal{P}_T(V) = R\frac{d}{dV}[\alpha - a - bE_0 + b^2\sigma^2/2]$, and $\mathcal{P}_{1/T}(V) = \frac{d}{dV}[\sigma^2/2R]$.

Along an isochore, the high T behavior is fixed by the linear term $T\mathcal{P}_T$, while the low T behavior is controlled by the T^{-1} term $T^{-1}\mathcal{P}_{1/T}$. From Eq. (3) one can also conclude that, in the harmonic Gaussian landscape, P along an isochore either is monotonically increasing with T (if $\mathcal{P}_{1/T} \leq 0$, simple liquid cases) or it has a minimum at $T = \sqrt{\mathcal{P}_{1/T}(V)/\mathcal{P}_T(V)}$ (if $\mathcal{P}_{1/T} > 0$, liquids with density anomalies) [23].

Equation (3) offers the possibility of understanding the landscape parameters responsible for density anomalies. Indeed, a Maxwell relation states that a density maximum state point (i.e., a point where $\partial V/\partial T|_P = 0$) is simultaneously a point at which the T dependence of P along an isochore has a minimum ($\partial P/\partial T|_V = 0$). Hence, the condition for the existence of density maxima, from Eq. (3), is that $P_{1/T} > 0$ which, in the PEL formalism, corresponds to $d\sigma^2/dV > 0$. Thus, in normal liquids, in the V range where liquid states exist, $d\sigma^2/dV$ must always be negative. On the contrary, liquids with density anomalies must be characterized by a V range where σ^2 increases with V [24].

The harmonic Gaussian landscape also elucidates the relation between density anomalies and the existence of a liquid-liquid critical point. Figure 1 schematically compares $P(T, V)$ along three different isochores: at the volume at which σ^2 is a minimum, $V = V_{\sigma^2_{\rm min}}$, and at two other V values, respectively, below and above $V_{\sigma^2_{\rm min}}$. In the harmonic Gaussian landscape P along the $V_{\sigma^2_{\rm min}}$ isochore increases linearly with T, since, by construction, $\mathcal{P}_{1/T}(V) = 0$ and $\mathcal{P}_T > 0$. For $V < V_{\sigma^2_{\rm min}}$, P decreases on cooling, since $\mathcal{P}_{1/T}(V) < 0$. The opposite trend is observed for $V > V_{\sigma^2_{\rm min}}$. An isothermal cut of the three isochores shows the corresponding $P(V)$ curves. At high T, where the linear T term is dominant, $P(V)$ is monotonically decreasing with V, while at low T the $P(V)$ isotherm is not monotonic, indicating the presence of a region of instability (negative compressibility). As a result, one must conclude that a critical point exists at an intermediate T, which can be accessed if no other mechanism (as, for example, crystallization or glass transition) preempts its observation.

We now compare the harmonic Gaussian landscape predictions with an extensive study of the PEL of one of the most widely studied models for water, the extended simple-point charge (SPC/E) [25]. SPC/E is able to reproduce water density anomalies. The PEL for this model has been studied in some detail previously [16,26]. We simulated a system of 216 water molecules with classical molecular dynamics (MD) in the NVE ensemble. We studied 45 different state points in supercooled states, for times longer than several α-relaxation times. Long range forces have been modeled via the reaction field technique. The integration time step was 1.0 fs. Results are averaged over 100 different independent trajectories for each state point. From each of the 100 trajectories we extracted about 30 configurations and calculated, via conjugate gradient techniques with 10^{-15} tolerance, the local minima (the so-called inherent structures) and their energies $e_{\rm IS}$. The vibrational density of states in the local minima has been calculated by diagonalizing the Hessian (the matrix of second derivatives of the potential). This procedure produces 3000 (30 × 100) distinct minima for each of the 45 studied state points, allowing the statistical error to be smaller than the symbol size. The resulting extremely accurate determination of $\sum_{i=1}^{6N-3} \ln[\omega_i(e_{\rm IS})]$, of the T dependence of $\langle e_{\rm IS}\rangle$, and of the configurational entropy $S_{\rm conf}$ [15]—a measure of the logarithm of the number of explored PEL basins—is crucial when accurate V derivatives of the PEL parameters are required, as in the present case. Procedures for the evaluation of the PEL parameters for the harmonic Gaussian model have been worked out [14,15,21,22]. From numerical evaluation of the T dependence of $\langle e_{\rm IS}\rangle$ and $S_{\rm conf}$ it is possible (i) to provide evidence that the Gaussian landscape correctly describes the SPC/E simulation data and (ii) to calculate, with a fitting procedure, σ^2, E_0 and α. The basin shape parameters a and b are calculated from the

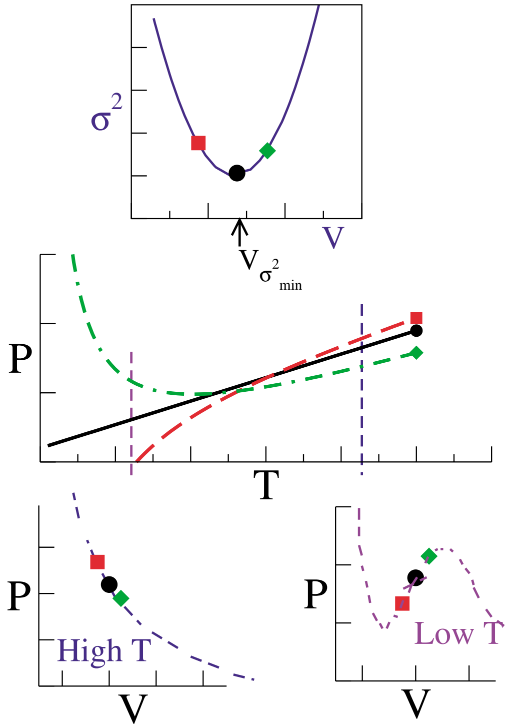

FIG. 1 (color online). Schematic explanation of the connection between a minimum in $\sigma^2(V)$ and a liquid-liquid critical point. Square, circle, and diamond indicate, respectively, a V smaller than, equal to, and larger than $V_{\sigma^2_{\rm min}}$. The central panel shows the corresponding isochores. Note that, as shown in Eq. (3), P increases (decreases) on cooling when $d\sigma^2/dV > 0$ (< 0). The bottom panels report the corresponding high and low T isotherms. At low T an unstable van der Waals loop appears.

$e_{\rm IS}$ dependence of the vibrational density of states, evaluated at the IS, i.e., by a linear fit of $\sum_{i=1}^{6N-3}\ln[\omega_i(e_{\rm IS})]$ vs $e_{\rm IS}$. The parameters E_0 and σ^2 are evaluated via a linear fit of $\langle e_{\rm IS}(T)\rangle$ vs T^{-1}. The parameter α is calculated by fitting the T dependence of $S_{\rm conf}$ [15,22].

Figure 2 shows the V dependence of the landscape parameters (α, E_0, σ^2) for nine different volumes and contrasts it with the behavior characteristic of simple liquids [27]. The total number of states α decreases on compressing the system, a feature common to all simple liquid models studied so far [15,22]. The V dependence of the energy scale E_0 is also analogous to the one found in simple liquid models. Indeed E_0 first decreases on compression, corresponding to the progressive sampling of the most attractive part of the potential; then it starts to increase due to the sampling of the repulsive part of the potential at short intermolecular nearest neighbor distances. As expected on the basis of the previous discussion, the V dependence of σ^2 shows instead elements which are not observed in simple liquid models, where σ^2 decreases monotonically on increasing V. In the SPC/E case, the variance shows a clear minimum around $V_{\sigma^2_{\rm min}} = 15$ cm^3/mol (i.e., at density $\rho = 1.2$ g/cm^3) and hints of a maximum at $V = 20$ cm^3/mol ($\rho = 0.9$ g/cm^3). Between 15 and 20 cm^3/mol, SPC/E water exhibits density anomalies. The increase of σ^2 for $V > V_{\sigma^2_{\rm min}}$ can be attributed to the fact that the system can explore new configurations, characterized by the presence of hydrogen bonds. The formation of such bonds requires a large local volume, and it is severely hampered at high density. These new accessible states widen the variance of the $\Omega(e_{\rm IS})$ distribution, producing a range of V values where $d\sigma^2/dV$ is positive. When V has increased to about 20 cm^3/mol the system has become mostly composed of a network of open linear hydrogen bonds and there are no more mechanisms available to increase the variance.

The actual location of the critical point, which will depend on all landscape properties, can be calculated according to Eq. (3). For the SPC/E harmonic Gaussian landscape, the resulting phase diagram is shown in Fig. 3. The density maxima locus retracing at low densities is consistent with the existence of a volume beyond which the liquid returns to normal (i.e., with $d\sigma^2/dV < 0$). The T of maximum density (TMD) locus at large pressures terminates along the liquid-liquid spinodal, as predicted by thermodynamic consistency [29]. Figure 3 also show the TMD line evaluated directly from the MD $P(V,T)$ data. This curve, which properly includes anharmonic contributions, shows that anharmonicities do not change

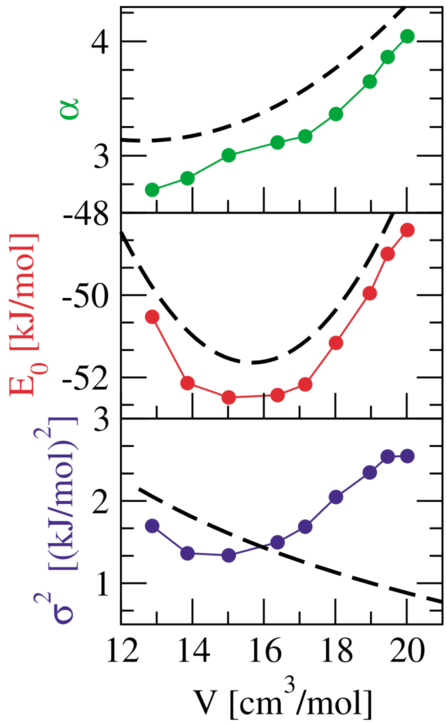

FIG. 2 (color online). Volume dependence of the PEL parameters for the SPC/E potential. Dashed lines indicate the trends expected for simple liquids [27].

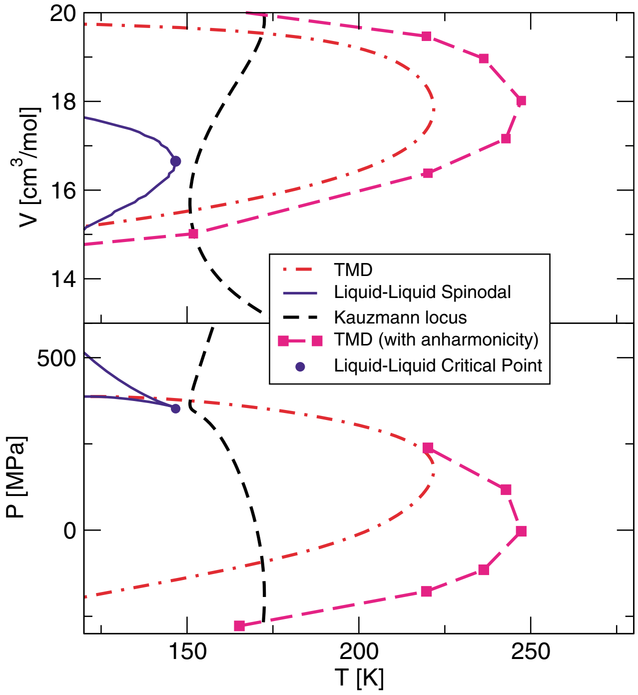

FIG. 3 (color online). Harmonic Gaussian landscape phase diagram for the SPC/E potential, including the TMD line, the liquid-liquid critical point with the associated spinodal lines, and the Kauzmann locus. Lines below the Kauzmann locus have no physical meaning, since they correspond to states with negative $S_{\rm conf}$. They are drawn here to visualize the termination of the TMD line and the relative position of the critical point respect to the Kauzmann locus. Squares indicate the TMD as evaluated directly from the MD calculations. As discussed in the text, adding the anharmonic contributions in the theoretical calculation would move the liquid-liquid critical point into the physically meaningful $S_{\rm conf} > 0$ region.

the topology but merely shift the TMD curve up about 25 K in T and down 160 MPa in P. The location of the liquid-liquid critical point for the SPC/E potential is estimated to be between ≈ 140 and 175 K and between ≈ 185 and 340 MPa, in agreement with previous predictions [30].

One of the powerful features of the PEL formalism is the possibility of simultaneously evaluating the EOS and S_{conf}. This offers the unique possibility of evaluating, within the chosen landscape model, the theoretical limit of validity of the low T extrapolations. In the present case, the limit set by the condition $S_{\mathrm{conf}} = 0$ defines a Kauzmann curve $T_K(P, V)$ below which the above EOS is no longer valid. The $T_K(P, V)$ locus is also indicated in Fig. 3. The TMD locus crosses the Kauzmann locus very close to its reentrance, as recently predicted by Speedy [31]. It is interesting to observe that the location of the liquid-liquid critical point is within the glass state and hence technically does not exist in the harmonic Gaussian approximation. When anharmonic contributions are taken into account, the critical point moves into the $S_{\mathrm{conf}} > 0$ region, suggesting that the liquid-liquid critical point could be a real feature of the SPC/E EOS. If this were the case, the possibility of observing a liquid-liquid critical point in this model would be hampered only by the extreme slowing down of the dynamics at low T and, in principle, by crystallization [32].

In this Letter we have shown that, in the harmonic Gaussian landscape model, density anomalies are a sufficient, but not a necessary, condition for the existence of a liquid-liquid critical point. Anharmonicities do not alter the picture and can be taken properly into account if necessary. Instead, the Gaussian hypothesis is crucial, and models with a different distribution $\Omega(e_{\mathrm{IS}})$ may produce density anomalies in systems without any liquid-liquid critical point [33]. Also, high-temperature fluid-fluid transitions [34] cannot be described by this formalism, which is applicable only to supercooled states. Still, the generality of the Gaussian distribution, rooted in the central limit theorem, strongly supports the possibility that what we learn studying the Gaussian landscape applies to water.

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