

Correspondence between phase diagrams of the TIP5P water model and a spherically symmetric repulsive ramp potential with two characteristic length scales

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We perform molecular dynamics simulations of the TIP5P water model and derive the physical parameters for a simple two-scale repulsive ramp potential model. We find that the regions of anomalous behavior in the phase diagrams of both systems can be mapped onto each other if (i) pressure P and temperature T are replaced by $T-T_C$ and $P-P_C$, respectively, where (T_C, P_C) are the coordinates of the liquid-liquid critical point of the corresponding system; and (ii) a single ramp particle corresponds effectively to two TIP5P molecules. We present heuristic arguments supporting point (ii). We also argue that the waterlike anomalies in the ramp potential are due to the ability of the particles to reproduce, upon compression or heating, the migration of water molecules from the second shell to its first shell.

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Liquid water is peculiar as reflected by its thermodynamic and dynamic anomalies [1,2], such as the density decrease upon isobaric cooling (density anomaly) and the increase of diffusivity upon isothermal compression (diffusion anomaly). It has been proposed that these anomalies may arise from a liquid-liquid critical point (LLCP) in the deeply supercooled state of water [3]. Several other liquids (e.g., silica, silicon, carbon, and phosphorous) with local tetrahedral order [4–6] also may show waterlike anomalies. These anomalies of water and the LLCP can be reproduced by simple liquids interacting via core-softened spherically symmetric potentials which lack the strong orientational interaction expected in tetrahedral liquids [7–15].

Water also possesses structural anomalies which occur when metrics describing both translational and orientational order decrease upon compression, as found in both the extended simple point charge (SPC/E) and TIP5P (five point transferable intermolecular potential) water models [2,16]. Water's structural anomaly is also reproduced by a family of core-softened spherically symmetric potentials possessing two characteristic length scales σ_0 and σ_1 [see the ramp potential in Fig. 1(a)] [12]. In order to exhibit a waterlike structural anomaly, the ratio $\lambda \equiv \sigma_0/\sigma_1$ must lie within a small interval around 0.62, the ratio of the distances to water's first and second neighbor shells, 0.28 nm/0.45 nm [12].

A quantitative connection between the ramp potential and water's pair potential has not been established, as well as the relation between the regions of anomalies in their respective phase diagrams. In this work, we show that the effective pair potential derived from the TIP5P water model [17] can be approximated by a two-scale spherically symmetric repulsive ramp potential, allowing us to assign physical units to the temperature and pressure of the ramp model. We perform molecular dynamics simulations using both the TIP5P and ramp potentials and compare the regions of anomalies in the corresponding phase diagrams. We find that the regions of anomalies in both phase diagrams are *quantitatively* similar if (i) pressure P and temperature T are measured in terms of $T-T_C$ and $P-P_C$, respectively, where (T_C, P_C) are the coor-

dinates of the LLCP of the corresponding system; and (ii) a ramp particle corresponds effectively to two TIP5P molecules. We present quantitative arguments supporting point (ii) and provide a simple picture to explain the similarities observed in the TIP5P and ramp potentials. A ramp liquid particle corresponds *effectively* to two water molecules, one molecule plus 1/4 of each of its four neighbors. The waterlike anomalies in the ramp potential are due to the ability of the particles to reproduce, upon compression or heating, the migration of water molecules from the second shell to its first shell.

The TIP5P model is a well-known water model and its parameters are defined in physical units, so values of P and T from simulations can be compared directly with experiments [17]. Instead, thermodynamic properties in the ramp potential are given in terms of potential parameters, such as $\{\sigma_0, U_0\}$, and the particle mass, m . To compare the phase diagrams of the ramp potential to that of the TIP5P model, we will define σ_0 and U_0 in units of “nm” and “kcal/mol,” respectively, and m in units of “g/mol.” We do this by calculating $U_{\text{eff}}(r)$, the effective spherically symmetric pair potential between water molecules from the TIP5P model simulations. $U_{\text{eff}}(r)$ is obtained from the oxygen-oxygen pair correlation function $g(r)$, by solving the Ornstein-Zernike equation, and using the hypernetted chain approximation [18]. The resulting $U_{\text{eff}}(r)$ depends on T and density ρ [19], but has no significant change for different state points in the anomalous region. For the TIP5P model, the range of anomalies is approximately $220 \text{ K} < T < 320 \text{ K}$ and $0.90 \text{ g/cm}^3 < \rho < 1.16 \text{ g/cm}^3$ [16]. We select a state point located in the middle of the anomalous regions, at $T=280 \text{ K}$ and $\rho = 1.00 \text{ g/cm}^3$, and calculate $g(r)$ and $U_{\text{eff}}(r)$ [see Fig. 1(b) and Fig. 1(c)]. We find that $U_{\text{eff}}(r)$ is similar to the effective pair potential obtained from the experimental $g(r)$ [18], and shows a hard-core-like steep repulsion at $r \approx 0.26 \text{ nm}$ and an approximately linear repulsive region covering the distance spanned by the second shell of a central water molecule, approximately $0.32 \text{ nm} < r < 0.45 \text{ nm}$. The shallow minimum at $r=0.28 \text{ nm}$ is caused by hydrogen-bonding attraction

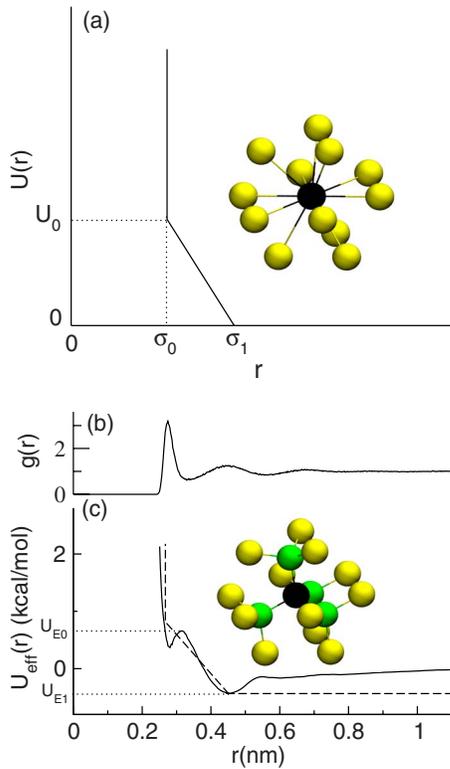


FIG. 1. (Color online) (a) The two-scale spherically symmetric repulsive ramp potential: σ_0 corresponds to the hard-core distance, and σ_1 characterizes a softer repulsion range that can be overcome at high P and T . The central ramp particle (black) and its twelve nearest neighbors (yellow) form a hcp crystal structure in a range of densities corresponding to the density anomaly. (b) The pair correlation function, $g(r)$, and (c) spherically symmetric effective potential, $U_{\text{eff}}(r)$, from the simulations using the TIP5P model at $T = 280$ K and $\rho = 1.00$ g/cm³ (solid line). For hexagonal ice, the twelve neighbors (yellow) in the second shell of the center water molecule (black) also has a hcp structure while the four nearest neighbors (green) in the first shell are located in the corner of a tetrahedron. $U_{\text{eff}}(r)$ can be approximated by a ramp potential (dashed lines). By calculating the integral of $g(r)$ for $r \leq \sigma_0$ we find that the hard core of the ramp particle roughly incorporates two water molecules (see also Fig. 2).

and corresponds to the first peak of $g(r)$, while the minimum at $r = 0.45$ nm [$U_{E1} \equiv U_{\text{eff}}(0.45 \text{ nm}) = -0.45$ kcal/mol] corresponds to the second peak of $g(r)$. $U_{\text{eff}}(r)$ also shows a maximum at $r \approx 0.32$ nm [$U_{E0} \equiv U_{\text{eff}}(0.32 \text{ nm}) = 0.66$ kcal/mol] that corresponds to the first minimum of $g(r)$.

Figure 1(c) also shows that a ramp potential is a good approximation to $U_{\text{eff}}(r)$. In the figure we set $\sigma_1 = 0.45$ nm and define the ramp part of the potential such that it intersects the plot of $U_{\text{eff}}(r)$ at $(U_{E0} + U_{E1})/2$. The intersection of the ramp part of the potential with the hard core of $U_{\text{eff}}(r)$ is used to define U_0 and σ_0 . This results in $\sigma_0 = 0.267$ nm, which is located between 0.28 nm, the first peak position of $g(r)$ and 0.26 nm, roughly the infinite repulsion part of $U_{\text{eff}}(r)$. Therefore, $\lambda \equiv \sigma_0/\sigma_1 = 0.593$ and $U_0 = U_{\text{eff}}(\sigma_0) - U_{\text{eff}}(\sigma_1) = 1.31$ kcal/mol. U_0 is approximately the energy barrier that water molecules need to overcome to migrate from the second shell to the first shell positions in terms of

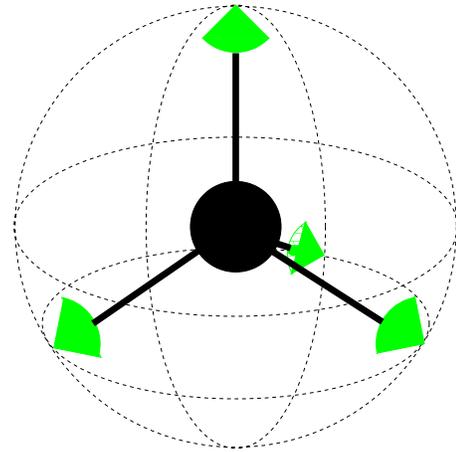


FIG. 2. (Color online) Sketch of a water molecule and 1/4 of each of its four nearest neighbors in a tetrahedral arrangement. Only oxygen atoms are shown for clarity. Mass of this unit corresponds effectively to the mass of a spherically symmetric ramp particle. The hexagonal ice [the low pressure crystal of water, Fig. 1(c)] can be obtained by combining these units in a hcp lattice [the low pressure crystal of the ramp potential model, Fig. 1(a)]. We notice this figure is in the spirit of the Walrafen pentamer [27] with the difference that the former consists of only two water molecules.

the effective potential. It is also roughly the energy that ramp particles need to overcome to reach the hard-core distance.

To define m in physical units, we argue that a spherically symmetric ramp particle [a particle interacting via ramp potential of Fig. 1(a)] has an effective mass corresponding to the mass of two water molecules. This is based on the crystalline phases of water (hexagonal ice) and ramp potential (hcp) at low pressures (see Fig. 1). The hexagonal ice can be formed by combining units such as that shown in Fig. 2. To form the hexagonal ice, such units must form a hcp network [see Fig. 1(c)]. Therefore, if the crystalline structure of the ramp potential model is identified with that of hexagonal ice, a ramp particle must be identified, on average, to the unit shown in Fig. 2. The mass of a water molecule is $m_w = 18$ g/mol; thus, the mass of a ramp particle is $m \approx (1 + 4 \times 1/4)m_w = 36$ g/mol. Alternatively, the present argument implies that the number density of the ramp potential model corresponds to twice the number density of water, and this will be relevant when comparing the pressures of the ramp and TIP5P models [20]. To test the idea that a ramp particle corresponds approximately to two water molecules, we calculate the average number of neighbors, N_0 , that a water molecule has within a distance of $r < \sigma_0 = 0.267$ nm. Using the $g(r)$ from Fig. 1 we obtain $N_0 \equiv 4\pi n \int_0^{\sigma_0} r'^2 g(r') dr' \approx 1$ (here, n is the number density), in agreement with our view. The correspondence between one ramp particle and two water molecules is also supported by computer simulations of the ramp potential with $\lambda = 0.581$ and an attractive part [10,11]. Such a ramp potential model has both liquid-gas (LG) and liquid-liquid (LL) critical points. Application of the values for σ_0 , U_0 , and m that we use here to the data from [10,11] results in $\rho_{LG} \approx 0.314$ and $\rho_{LL} \approx 1.188$ g/cm³. These values approximately coincide with the experimental critical density of water $\rho_{LL} \approx 0.322$ [21] and the LL critical density of TIP5P water $\rho_{LL} \approx 1.13$ g/cm³ [22].

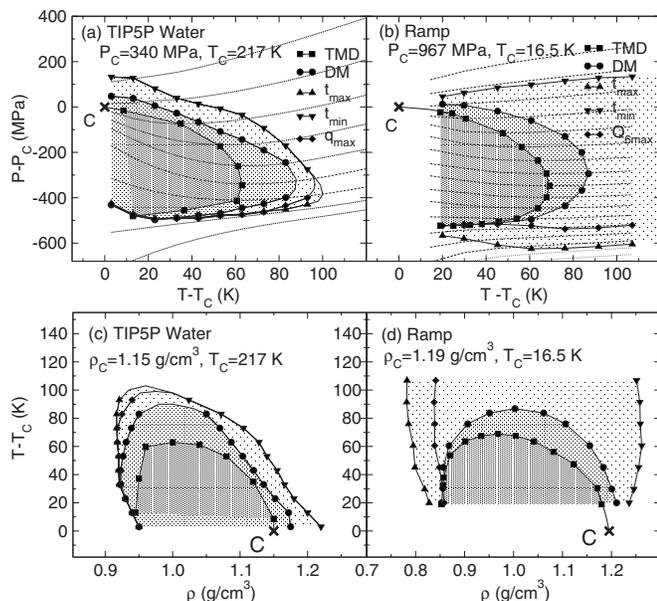


FIG. 3. (a) Three anomalous regions of TIP5P water in a modified P - T phase diagram. The dashed lines are the isochores with density $\rho = 1.20, 1.16, 1.12, 1.08, 1.04, 1.00, 0.96, 0.92, 0.88$ g/cm³ from top to bottom. Density anomaly region (dark shaded) is defined by temperature of maxima density (TMD, filled squares) lines, inside which the density increases when the system is heated at constant pressure. Diffusion anomaly region (medium shaded) is defined by the loci of diffusion maxima-minima (DM, filled circles), inside which the diffusivity increases with density at constant T . Structural anomaly region (light shaded) is defined by the loci of translational order minima (t_{\min} , filled down triangles) and maxima (t_{\max} , filled up triangles), or orientational order maxima q_{\max} (filled diamonds, Q_6 max for ramp liquid), inside which both translational and orientational orders decrease with density at constant T (see Refs. [2,12,16] for details). Here t quantifies the tendency of molecular pairs to adopt preferential separations, and q quantifies the local tetrahedrality of water (Q_6 quantifies the local orientational order of twelve nearest neighbors in the first shell of a ramp particle). (b) Anomalous regions for the ramp liquid: here the values of P and ρ are doubled in order to compare with the corresponding values of water [see text]. The dashed lines are the isochores with density $\rho = 1.33, 1.28, 1.23, 1.18, 1.14, 1.09, 1.05, 1.02, 0.98, 0.94, 0.91, 0.88, 0.85, 0.82, 0.79, 0.77, 0.74$ g/cm³ from top to bottom. (c),(d) are the anomalous regions in the T - ρ phase diagrams. “C” is the location of the LLC.

To compare the regions of anomalies in the phase diagrams of the TIP5P and ramp potentials, we first obtain the LLC coordinates (P_C, T_C, ρ_C) . The LLC in the TIP5P model is accessible in molecular dynamics (MD) simulations and is located at $T_C = 217$ K, $P_C = 340$ MPa, and $\rho_C = 1.13 \pm 0.04$ g/cm³ [23,24]. Instead, for the ramp potential of Fig. 1(a), the extrapolated LLC is located at temperatures below those accessible in simulations [9]. In this case, the LLC can be located by extrapolating the isochores in the P - T phase diagram to low- T (the isochores cross each other at the LLC). This procedure indicates that the LLC is located at $T_C = 16.5$ K, $P_C = 967$ MPa, and $\rho_C = 1.19$ g/cm³.

Figure 3 shows the phase diagrams of the TIP5P and ramp potential models, obtained by MD simulations (for details

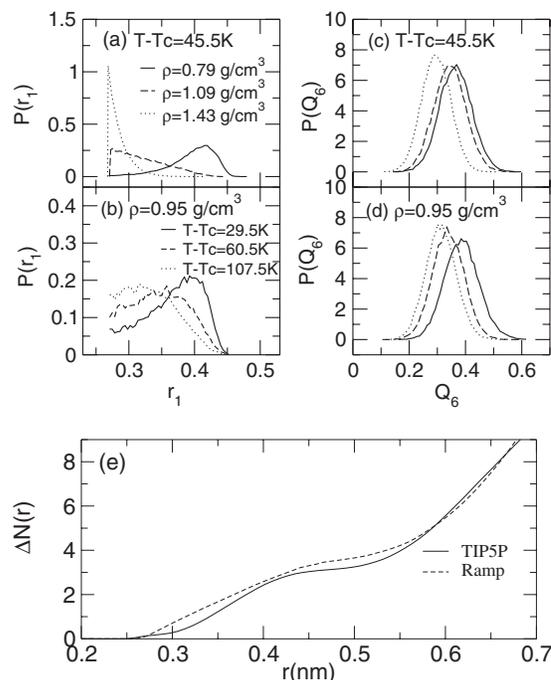


FIG. 4. Probability distribution of the distance r_1 of a central ramp particle and its nearest neighbor at (a) constant T and (b) constant ρ . (c),(d) Probability distribution of orientational order parameter for a ramp potential particle corresponding to panels (a) and (b), respectively. Upon heating or compression, ramp particles move from the soft-core distance toward the hard-core distance and the orientation order parameter decreases. Similar structural changes occur in water [16]. (e) Increase in the number of neighbors, $\Delta N(r) \equiv N(r)|_{\rho_1} - N(r)|_{\rho_0}$, where $\rho_1 = 0.88$ g/cm³ and $\rho_0 = 1.08$ g/cm³, for the TIP5P and ramp potentials. We doubled the values of $N(r)$ and $\Delta N(r)$ obtained from the simulations using the ramp potential model (see text).

see [9,12,16]). To emphasize the quantitative similarities of these diagrams we place the origins of P and T axes at the LLC of the corresponding models. In both models, the density anomaly region is within the diffusion anomaly region, which is enclosed by the structure anomaly region. A comparison of Figs. 3(a) and 3(b), or Figs. 3(c) and 3(d), shows *quantitative* similarities in the regions of anomalies of both models. For example, the density anomaly region covers approximately the ranges $-500 < P - P_C < 0$ MPa, $T - T_C < 60$ K, and $0.9 < \rho < 1.15$ g/cm³ for both models. Similarly, the diffusion anomaly region covers approximately the ranges $-500 < P - P_C < 0$ MPa, $T - T_C < 90$ K, and $0.9 < \rho < 1.2$ g/cm³ for both models. The structural anomaly regions show some differences, extending to higher- T for the ramp potential model than for the TIP5P model.

A possible reason for the *quantitative* similarities in the regions of anomalies of water and ramp potential model is that this model is able to reproduce *quantitatively* the observed migration of water molecules from the second shell toward the first shell upon compression or heating [16,25,26]. We discuss first the probability distribution, $P(r_1)$, of the distance between a ramp particle and its nearest neighbor. Figure 4(a) shows the evolution of $P(r_1)$ upon iso-

thermal compression. As density increases, the maxima of $P(r_1)$ shifts from $r=0.42\text{ nm}\approx\sigma_1$, at low density, to $r=0.267\text{ nm}=\sigma_0$, at high density. Figure 4(b) shows that a similar but less pronounced changes in $P(r_1)$ occur upon isobaric heating. Thus, upon compression or heating, particles move from the soft-core distance (corresponding to water's second shell) toward the hard-core distance (corresponding to water's first shell) of the ramp potential. The probability distribution, $P(Q_6)$, of the orientational order parameter, Q_6 [12], of the ramp potential particles is shown in Figs. 4(c) (upon isothermal compression) and 4(d) (upon isobaric heating). Upon compression or heating, the maximum $P(Q_6)$ shifts to small values of Q_6 , i.e., orientational order decreases. Similar structural changes occur in water [16,25,26]. In particular, Figs. 4(a) and 4(b) and Figs. 4(c) and 4(d) can be compared with the corresponding Figs. 4(c) and 4(f) and Figs. 4(b) and 4(e) of Ref. [16] obtained for the TIP5P model. For a quantitative comparison of the structural changes in the ramp and TIP5P models, we calculate the number of neighbors, $N(r)$, as a function of the distance r from a central water molecule and/or ramp particle in both models. The increase of $N(r)$ with density, $\Delta N(r)$ in Fig.

4(e), shows similar change for both models. Thus, the ramp potential reproduces *quantitatively* the migration of water molecules from the second shell toward the first shell upon compression or heating.

In summary, our study makes a microscopic *quantitative* connection between a ramp potential and the TIP5P water model and shows that orientational interactions, such as hydrogen bonding, are not necessary to reproduce waterlike anomalous properties. In general, the ramp potential provides an understanding of the anomalous features of tetrahedral liquids. These features are caused by a large empty space around the tetrahedrally coordinated molecules, which is reduced as temperature and pressure increase. In the ramp liquid, this empty space is created by the repulsive soft core.

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