Confined of Anomalous Liquids in Nanoporous Matrices

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Using molecular dynamics simulations, we investigate the effects of different nanoconfinements on complex liquids—e.g., colloids or protein solutions—with density anomalies and a liquid-liquid phase transition (LLPT). In all the confinements, we find a strong depletion effect with a large increase in liquid density near the confining surface. If the nanoconfinement is modeled by an ordered matrix of nanoparticles, we find that the anomalies are preserved. On the contrary, if the confinement is modeled by a disordered matrix of nanoparticles, we find a drastically different phase diagram: the LLPT shifts to lower pressures and temperatures, and the anomalies become weaker, as the disorder increases. We find that the density heterogeneities induced by the disordered matrix are responsible for the weakening of the LLPT and the disappearance of the anomalies.

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Many experiments in recent years have shown that a number of liquids exhibit highly anomalous properties [1]. The data for liquid metals, metalloids, nonmetals, oxides, and alloys—including Ga, Bi, Te, S, Be, Mg, Ca, Sr, Ba, SiO2, P, Se, Ce, Cs, Rb, Co, Ge, Ge15Te85—colloids, protein solutions, organophosphates, such as triphenylphosphate (TPP), AY20 melts [(Al-O)40 − (Y-O)20], and water, reveal the presence of a temperature of maximum density (TMD) below which the density decreases under isobaric cooling [1]. In a number of these systems, such as P, TPP, and AY20 [2], it has been shown that a liquid-liquid phase transition (LLPT) exists and that it ends in a liquid-liquid critical point (LLCP) between two coexisting liquids of the same composition but different structure: the high density liquid (HDL) and the low density liquid (LDL). Data from experiments on silica, C, Se, Co, and water are consistent with a LLPT [3]. Here, we ask how the structure of the nanoconfinement may change the anomalous behavior of the liquid and affect the LLPT and the LLCP. This question is relevant across a wide range of nanotechnological applications, biological systems, and is of general interest for phase transitions in confined systems [4].

We model the liquid using two different potentials, (i) the Jagla ramp potential [5] and (ii) has a repulsive shoulder and an attractive well with energy minimum \(U_0\), with parameters chosen to fit a potential proposed in Ref. [7]. The interaction with NPs is given by a \(1/(r - r_0)\) power law. For both potentials, we perform simulations at constant number \(N\) of liquid particles, constant volume \(V\), and constant temperature \(T\), with periodic boundary conditions. For (i), we employ a discrete molecular dynamics (MD) algorithm by discretizing the linear ramp potential into steps, with \(\Delta U = U_0/8\) [8]. For (ii), we use a standard MD with a velocity Verlet integrator and the Allen thermostat [6].

We consider three different structures for the matrix: a perfect cubic lattice (CUBE); a cubic lattice with Gaussian distortions (DIST) with a standard deviation equal to 1/4th the separation between centers of NPs, which still preserves an approximately periodic and ordered structure of the confinement [Fig. 1(a)]; and a completely random (RND) configuration of NPs obtained by simulating a gas of hard spheres [Fig. 1(b)]. The volume fraction of NPs is \(x_{NP} = V_{NP}/V\), where \(V\) is the volume of the cubic simulation box and \(V_{NP} = N_{NP} 4\pi r_0^3/3\) is the volume inaccessible to the liquid. Our results here, if not otherwise indicated, are for liquid (i) confined by the matrix of \(N_{NP} = 64\) NPs with diameter \(D_{NP}/a = 3\) at \(x_{NP} = 24.5\%\) and \(V/a^3 = 20.6^3\). We control the density \(\rho = N/(V - V_{NP})\) of the liquid particles by changing \(N\) in the interval between 1845 and 3887. We take into account that the excluded volume rescales the pressure \(P\) by \((V - V_{NP})\). We find that the results for liquid (ii) are consistent in similar conditions.

For liquid (i), the bulk system displays a LLCP at \(k_B T_c^{bulk}/U_0 = 0.375\), \(P_c^{bulk} a^3/U_0 = 0.243\), and \(\rho_c^{bulk} a^3 = 0.37\) [5]. Figures 1(c) and 1(d) show simulated isochores for DIST and RND confinement, respectively, with the
manifests itself in the shrinking of the region between the spinodals in the $P$–$T$ plane. This shrinking is qualitatively consistent with that found for a model of water in a random hydrophobic pore-like confinement [11].

The region of density anomaly is bounded by the lines of the TMD and the temperature of minimum density (TminD) located by the extrema of the isochoros. In the bulk system, the TminD line for high densities is hindered by the glass temperature line and cannot be observed in the equilibrium liquid. Here, we observe that the periodic structure of the confinement can dramatically affect density anomaly manifestations. Compared to the bulk, confinement decreases TMD and increases TminD, shrinking the $T$ range of the density anomaly. The density anomaly is still well-defined in the DIST case, but it appears much less pronounced in the RND case. For a RND matrix of $N_{NP} = 19$ large confining NPs with diameter $D_{NP}/a = 5$ at $x_{NP} = 24.5\%$ and $V/a^3 = 20.6^3$, the TMD and TminD are completely absent (not shown).

To understand the origin of the different effects of the different confinements, we study the density of the liquid in the vicinity of NPs. We find that a layer of liquid adsorbs onto the NPs, as revealed by the fluid density profile $\rho_{NP-liq}(r)$ (Fig. 3). We understand the increase of density near the NP surface as a consequence of entropy maximization. By packing near the fixed NPs, the adsorbed...
necessary to build up the critical fluctuations. The shift is in the vicinity of the NPs. We find that large peaks near the minimum of $g_{\text{NP-liq}}(r)$, consistent with a tight packing of liquid between two concentric spheres with different radii 

$$R = 0.2a \quad \text{and} \quad R = 2.0a, 2.2a, \ldots, 8.0a \quad \text{(one such conical region is shown in dark red).}$$

The axis of the conical region is chosen at random 10000 times for each NP. $g_{\text{NP-liq}}(r)$ is computed by counting the number of liquid particles and local $K_T$ (dashed lines) shows large peaks near the minimum of $g_{\text{NP-liq}}(r)$. The results for different confinements are shifted horizontally for clarity. Inset: Schematic representation of calculation of $g_{\text{NP-liq}}(r)$ and local $K_T$ inside equal-volume ($\Delta W = 2.77a^3$) conical regions between two concentric spheres with different radii $R$ and $R + \Delta R$ centered at the NP (small yellow hemisphere in the middle), where $\Delta R = 0.2a$ and $R = 2.0a, 2.2a, \ldots, 8.0a$ (one such conical region is shown in dark red). The axis of the conical region is chosen at random 10000 times for each NP. $g_{\text{NP-liq}}(r)$ is computed by counting the number of liquid particles and local $K_T = [(n_i^2)/n^2] - 1][\Delta W/k_bT]$ from fluctuations of number of liquid particles $n$.

Liquid particles allow more free space to the the rest of the liquid, maximizing the entropy of the system (depletion effect). This result evokes a similar effect found for water at confining surfaces, regardless of the hydrophobic or hydrophilic interaction with the surface [12], and for hard-sphere fluids in contact with purely repulsive particles [13], showing that the increase of contact density is not related to specific interactions or anomalous behaviors and making a bridge between water and simple fluids.

We find that, by increasing randomness in the confinement, the probability of overlap of NP exclusion volumes increases and the depletion effect decreases. As a consequence, the density of liquid near the NPs decreases (Fig. 3). In addition, we analyze the density fluctuations and the associated measurable response function, the local isothermal compressibility $K_T$ (Fig. 3), of the liquid in the vicinity of the NPs. We find that $K_T$ is extremely small at the interface, consistent with a tight packing of liquid particles around the NPs. Near the first minimum of $g_{\text{NP-liq}}(r)$, $K_T$ is, instead, twice as high as in the bulk. A high local density causes the density increase of the LLCP (Fig. 2) because, when part of the liquid is adsorbed onto the NPs, an average liquid density larger than bulk is necessary to build up the critical fluctuations. The shift is more pronounced for CUBE and DIST confinement, with respect to RND, because the more ordered confinement, the larger the NP surface available for the depletion effect.

To better understand how confinement structure affects the physical properties of a liquid, we study the liquid’s local density distribution inside the confinement matrix. We identify the region not occupied by the NPs and partition it into disconnected cavities [inset Fig. 4(c)] based on the Delaunay tessellation algorithm described in Ref. [14]. We define the exclusion spheres concentric with NPs and gradually increase their radius $r_e$ with a small step $\Delta r_e = 0.1a$. We designate the space not occupied by exclusion spheres as void of size $r_e$ and denote it $\Omega(r_e)$. For...
$r_e = r_0$, $\Omega(r_0)$ is a connected set for both RND and DIST
conefinements. The volume of $\Omega(r_0)$ is equal to $V - V_{NP}$.

In DIST confinement, when $r_e > 4.1a$, $\Omega(r_e)$ breaks
into 64 small disconnected cavities, associated with 64
distorted cubic pockets formed by 8 adjacent NPs. The
volume $\omega_i$ of each pocket $i = 1, \ldots, 64$ is given by the
volume of all Delaunay tetrahedra comprising the corre-
responding pocket minus the volume occupied by the NPs
forming the pocket. We define the particle density of liquid in
each pocket $\rho_i \equiv N_i/\omega_i$, where $N_i$ is the number of
liquid particles inside pocket $i$. We find that the volumes $\omega_i$
are narrowly distributed, with the local liquid density
distribution $D_{DIST}(\rho_i)$ given by a Gaussian with variance
$\sigma_D^2$ [Fig. 4(a)].

In RND confinement, $\Omega(r_e)$ remains fully connected up
to $r_e = 4.2a$. As we increase $r_e$, small pockets break away
from the largest part of $\Omega(r_e)$ one by one. When $r_e = 5.4a$,
we count, for different random configurations, approximately
60 pockets, for which we calculate $\omega_i$ and $\rho_i$, finding a large variety of sizes and shapes. We compute
$D_{RND}(\rho_i)$ and find that in RND it can be approximated
with the sum of two Gaussian distributions: one similar to the
DIST case with $\sigma_{R1} = \sigma_D$ and the other resulting
from the heterogeneity of volumes $\omega_i$ of the pockets with
$\sigma_{R2} > \sigma_{R1}$ [Fig. 4(b)].

We hypothesize that in RND confinement, the observed
pressure $p_{RND}(T, \rho)$ results from averaging local pressures
in each pocket. At temperature $T$, we estimate $p_{RND}$ using the average of the $p_{DIST}(T, \rho_i)$ over all heterogeneous
pockets [Fig. 4(c)],

$$p_{RND}(T, \rho) = \int p_{DIST}(T, \rho + \rho \xi) \exp\left(-\frac{\xi^2/2\sigma_{R2}^2}{\sqrt{2\pi}\sigma_{R2}}\right) d\xi.$$  \hfill (1)

Due to averaging over different densities $\rho_i \equiv \rho + \rho \xi$, the
nonmonotonic subcritical isotherm $p_{DIST}(\rho)$ at $T =
T_{c}^{RND} < T_{c}^{DIST}$ becomes a monotonic critical isotherm
$p_{RND}(\rho)$ that closely fits the simulation results for the
RND confinement in the vicinity of the LLPT. Thus, our
averaging technique allows us to reproduce quantitatively
the differences we found when we compared DIST and
RND confinements; i.e., the critical temperature, pressure,
and density decrease [Fig. 2(a)] and density anomaly region
shrinks [Figs. 1(c) and 1(d)]. Thus, the presence of
density heterogeneity and the reduced depletion effect in the
RND confinement matrix give us the key to understand-
ing the effect of confinement structures. It is import-
tant to stress the differences of the effect of confinement on
the LLPT and the liquid-gas phase transition (LGPT).
While in both cases the critical temperature is significantly
reduced, the effects of random confinement and ordered
confinement are practically indistinguishable in the case of
LGPT. This is because in LGPT, the density of liquid
particles has a much smaller increase near NPs than in
LLPT. Thus, in LGPT, randomness does not lead to local
density heterogeneities, which produce a strong effect on
the LLPT.

In conclusion, we predict that anomalous liquids with a
LLPT retain their bulk phase diagram and density anom-
alies when they are confined in a porous matrix with an
ordered structure. Furthermore, when there is a small dis-
ortion of the confinement, the glass temperature is reduced
with respect to bulk, allowing the direct observation of the
TmntD locus. A strong depletion effect induces a large
increase of density in the vicinity of the NPs. The effect is
smaller when the confinement has a random structure.
Randomness induces heterogeneity in the local density,
which weakens the LLPT, narrows the LLPT coexistence
region, and washes out the density anomalies.

Although the anomalous liquids considered here are, in
principle, different from water, our results could qualita-
tively explain recent experiments for confined water, the
prototypical anomalous liquid. While the TmntD locus has
been observed in supercooled water under hydrophilic
confinement by the MCM-41 silica nanoporous matrix
[15], its absence has been reported in the hydrophobic
mesoporous material CMK [16]. MCM-41 forms a regular
matrix [15], but CMK consists of grains, each with a
disordered pore structure [16]. This suggests that the dis-
parity of results for different confinements may arise from
the different amount of disorder in the confining structures,
independent of the interaction details of the anomalous
liquid.

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