



Local density augmentation in neat supercritical fluids: the role of electrostatic interactions

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Abstract

Motivated by a recent study of Saitow et al. [Chem. Phys. Lett. 368 (2003) 209–214], computer simulations and dielectric analyses are used to explore the effect electrical interactions have on density augmentation in supercritical fluoroform. Simulations of 2-site models of fluoroform and ethane show that electrical interactions increase local densities but not dramatically. The density augmentation simulated in both fluids ($\Delta\rho_{\max} = 0.12\rho_c$ and $0.15\rho_c$) is much smaller than the value $\Delta\rho_{\max} \cong 0.5\rho_c$ deduced by Saitow et al. from Raman measurements. This discrepancy can be reconciled if the observed vibrational shifts reflect mainly dipolar interactions, an interpretation justified by ab initio calculations. © 2003 Elsevier B.V. All rights reserved.

1. Introduction

A characteristic feature of fluids near to their critical points is the presence of density inhomogeneities. In pure fluids, such inhomogeneities are most dramatically manifest in the divergence of many thermodynamic properties, brought about by the diverging size of density fluctuations. In dilute supercritical solutions additional inhomogeneity exists in the phenomenon of density augmentation – the presence of excess solvent density in the neighborhood of an attractive solute. These two forms of density inhomogeneity

are distinct [1,2]. Whereas critical phenomena in neat supercritical fluids reflect long-range *fluctuations* in solvent density, local density augmentation in supercritical solutions is an *average* behavior, which is primarily related to short-range interactions between the solute and solvent. In the case of large attractive solutes in small-molecule solvents, for example anthracene in ethane, spectroscopic experiments suggest local densities that average 2–5 times bulk solvent densities below the critical density [3,4]. These estimates are largely confirmed by computer simulations of simplified [4,5] and realistic [4,6,7] model solutions near the critical point. Computer simulations of neat supercritical fluids also indicate that the average density in the vicinity of a solvent molecule is greater than the bulk density,

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but the magnitude of the effect is found to be much smaller [8], amounting to only $\sim 20\%$ in (3-dimensional [9]) Lennard-Jones fluids [4,10]. Experimental data from vibrational frequency shifts observed in neat supercritical methane [11], ethane [12], and CO_2 [13] show little sign of density augmentation, in agreement with these simulation results. It therefore appears that a significant asymmetry in solute–solvent versus solvent–solvent interaction strength is required to generate substantial local density augmentation.

Recent results by Saitow et al. [14] appear to be at odds with this idea. These authors used Raman spectroscopy to measure the frequencies and line widths of the symmetric CF_3 stretch in neat fluoroform on the supercritical isotherm $T = 1.02 T_c$. From the nonlinear shifts of the frequency of this vibration with solvent density, Saitow et al. deduced local densities that were as much as a factor of two larger than bulk values at low densities. Noting that all previous studies reporting small or negligible density augmentation in neat fluids in-

volved only fluids of nonpolar molecules, they suggested that the long-range character of the electrostatic interactions present in fluoroform engender much greater augmentation than is found in nonpolar fluids.

In the present note we examine this suggestion using both computer simulations and general considerations of the possible relationships between spectral shifts and local densities in polar fluids. We first compare the local densities simulated using two simplified (diatomic) representations of the fluids fluoroform and ethane. We find that there is no pronounced difference in the local densities simulated for these two fluids. In keeping with past simulations, the extent of the density augmentation observed in both model fluids is modest. To explain the experimental observations of Saitow et al., we therefore examine the effect of electrical interactions on vibrational shifts in a polar fluid such as fluoroform. We find that if one assumes that the vibrational shifts are primarily sensitive to electrostatic rather than dispersive

Table 1
Summary of simulated properties of fluoroform and ethane (310 K)

#	P (MPa)	ρ (ρ_c)	N_1	N_2	$-U$ (kJ mol $^{-1}$)	$-U_{\text{el}}$ (kJ mol $^{-1}$)	$-U_{\text{LJ}}$ (kJ mol $^{-1}$)	F_{LJ} (10^{-4} a.u.)	F_{El} (10^{-4} a.u.)
<i>Fluoroform</i>									
1	3.47	0.24	1.7	6.1	3.90	1.90	1.99	-1.32	4.50
2	4.90	0.48	3.1	11.8	6.80	3.10	3.69	-2.44	7.33
3	5.40	0.67	4.1	16.4	8.85	3.86	4.99	-3.26	9.12
4	5.56	1.12	6.3	26.2	12.9	5.17	7.68	-5.04	12.2
5	5.86	1.32	7.1	30.0	14.3	5.62	8.72	-5.78	13.3
6	7.98	1.61	8.3	35.8	16.5	6.25	10.3	-6.96	14.7
7	17.6	1.95	9.9	42.8	19.2	6.99	12.2	-8.79	16.4
<i>Ethane</i>									
1	3.26	0.24	1.5	5.9	2.45		2.45	-1.21	
2	4.97	0.48	3.0	12.0	4.83		4.83	-2.49	
3	5.61	0.76	4.6	18.6	7.36		7.36	-3.96	
4	5.75	1.01	5.9	24.4	9.64		9.64	-5.44	
5	5.85	1.22	6.8	28.4	11.0		11.0	-6.31	
6	8.60	1.65	8.7	37.2	14.2		14.2	-8.85	
7	22.2	2.01	10.4	45.0	17.2		17.2	-12.1	

P and ρ are the simulated pressure and density. N_1 and N_2 are the center of mass coordination numbers $N(R)$ with $R_1, R_2 = 6.5, 10.5$ Å for fluoroform and 6.8, 11 Å for ethane (the distances of the 1st two minima in $g(r)$ at high density). U , U_{LJ} , and U_{el} are the interaction energy between a central molecule and the remaining fluid and the contributions to this energy resulting from Lennard-Jones and electrical terms in the potential. F_{LJ} and F_{El} are the Lennard-Jones and electrical contributions to the bond force, the component of the net force on a molecule projected along the bond direction. (F is defined to be positive for a force that would tend to stretch the bond. 1 a.u. = 8.24×10^{-8} N.) Statistical uncertainties in these quantities are less than $\pm 5\%$ in all cases.

interactions, the observed shifts are completely consistent with the augmentation observed in the simulations.

2. Simulations of density augmentation

To explore what differences in local densities might result from electrostatic interactions, we compare simulated results for models of neat fluoroform and ethane using 2-site models previously tuned to reproduce the experimental critical points and liquid–vapor coexistence curves of these fluids [15,16]. Both models are of the site–site Lennard-Jones type; the primary difference between them is the presence of site charges of $\pm 0.275e$ in the fluoroform model ($\mu = 2.2$ D) absent in the ethane case. Isothermal, isobaric simulations were carried out on 1000-molecule samples of each fluid at a

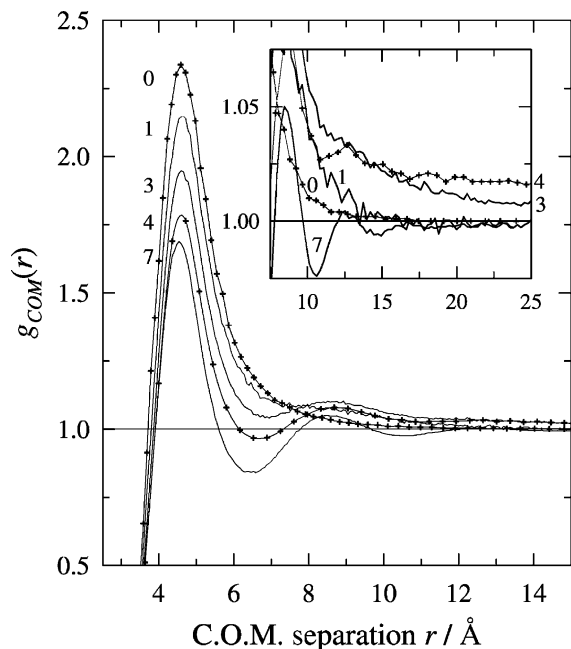


Fig. 1. Center-of-mass radial distribution functions in fluoroform at several densities. ‘0’ denotes the $\rho = 0$ limit and the remaining numbers refer to the densities listed in Table 1 (#1 = 0.25, #3 = 0.71, #4 = 1.1, and #7 = $2.0\rho_c$). Data from #0 and #4 are drawn as connected points and #1, 3, and 7 as simple lines for contrast. The inset shows these same data in a manner that emphasizes the tails of the distribution functions.

temperature of 310 K and series of seven pressures spanning the density range 0.25 – $2.0\rho_c$ (see Appendix A for details). Some of the relevant equilibrium data collected in these simulations is gathered in Table 1.

The simulated solvation structure is characterized in Figs. 1 and 2. Fig. 1 shows center-of-mass radial distribution functions $g_{\text{com}}(r)$ observed in the fluoroform system. The distributions in ethane are quite similar and are not shown. The curve marked ‘0’ is the gas-phase result, $g_{\text{com}}(r) = \langle \exp\{-u(r, \Omega)/k_B T\} \rangle_{\Omega}$, where $u(r, \Omega)$ represents the pair potential and Ω the relative angles between two molecules [4]. Evolution from this gas-phase limit to the oscillatory structure characteristic of dense liquids, as well as the appearance of long-range tails in these functions for $\rho \sim \rho_c$ (inset) is

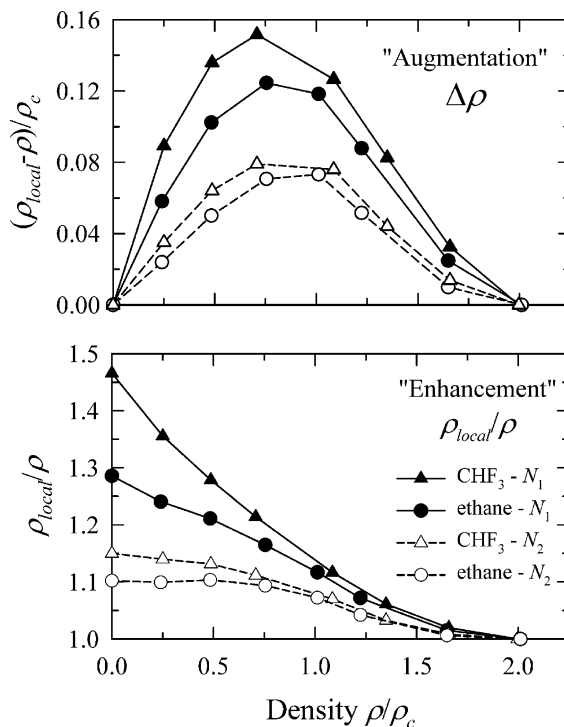


Fig. 2. Two representations of the local densities simulated in fluoroform (triangles) and ethane (circles). The top panel displays the density augmentation $\Delta\rho \equiv \rho_{\text{local}} - \rho$ and the bottom panel the density enhancement ρ_{local}/ρ . Filled and open symbols denote densities determined from the numbers of molecules in the 1st (N_1) and 1st+2nd (N_2) solvation shells of a central molecule.

apparent in these data. Such features are typical of what has been observed in other supercritical fluids at temperatures near to T_c [17–19].

Coordination numbers N are obtained by integrating $g_{\text{com}}(r)$ out to some specified distance R . Values of N_1 and N_2 , the coordination numbers of the 1st and (1st + 2nd) solvation shells (Table 1) are quite similar in the two model fluids. In both cases there are roughly 10 and 35 molecules in the 1st and 2nd solvation shells at $\rho = 2\rho_c$. Also shown in Table 1 are the average interaction energies U of a central molecule with the remaining fluid and the Lennard-Jones (U_{LJ}) and electrical (U_{El}) components of this energy. At the highest densities studied the net interaction energies are comparable in the two fluids, but at the lowest densities the fluoroform energies are 40–60% larger than in ethane, primarily due to the additional attraction provided by electrical interactions.

Local densities are defined in terms of coordination numbers by assuming an equality between local and bulk densities at a reference density $\rho_{\text{ref}} = 2\rho_c$

$$\rho_{\text{local}}(\rho) \equiv \frac{N(\rho)}{N(\rho_{\text{ref}})} \rho_{\text{ref}}. \quad (1)$$

By defining local densities in this manner, the ‘density augmentation’, $\Delta\rho \equiv \rho_{\text{local}} - \rho$, and ‘density enhancement’, ρ_{local}/ρ , reported here exclude the density buildup near a central molecule caused by packing constraints high densities. That is, the structural considerations making $g_{\text{com}}(r)$ significantly greater than unity at high densities are approximately removed by this definition of ρ_{local} , such that the excess densities discussed here mainly reflect the attractive interactions important at lower densities.

Fig. 2 shows the values of $\Delta\rho$ and ρ_{local}/ρ in the region of the 1st and 1st + 2nd solvation shells of molecules in fluoroform and ethane. The simulations predict augmented densities in the 1st solvation shell which are maximal for bulk densities of ~ 0.7 – $0.8\rho_c$. The values of $\Delta\rho_{\text{max}}$ are 0.16 and $0.13\rho_c$ for fluoroform and ethane, respectively. In terms of ρ_{local}/ρ , both fluids show a monotonic decrease in the density enhancement in the 1st solvation shell from the gas-phase limits ($\rho_{\text{local}}/\rho)_0 = 1.47$ in fluoroform and 1.29 in ethane. When

the density in the larger region encompassing the 1st + 2nd solvation shells is considered, both measures of the density excess decrease markedly. Most importantly, in keeping with the observations of Saitow et al. [14], we do find greater augmentation in the polar fluid fluoroform compared to the nonpolar fluid ethane. Presumably, the electrical contributions which render the solvation energies of fluoroform substantially greater than those of ethane at low densities give rise to this difference. But the simulated difference between ethane and fluoroform is small and far from sufficient to explain the large values of excess densities deduced from experimental Raman data in fluoroform, $\Delta\rho_{\text{max}} \sim 0.5\rho_c$. The simulations in both fluoroform and ethane show only the modest degree of augmentation that has come to be expected for neat supercritical fluids. Thus, the present simulations do not support the dramatic effect of polar interactions suggested by the experimental data and analysis of Saitow et al.

3. Dielectric models of spectral shifts

The disagreement between simulation and experiment concerning density augmentation in neat fluoroform could be due to lack of realism in the simulations or alternatively to misinterpretation of what the experimental data implies about local densities. It must be remembered that experiments do not measure densities directly, they do so only indirectly using some observable property sensitive to local density. The difficulty with interpretation of experimental data is that the exact relation linking the observable to density is usually not known with certainty. In the present case, Saitow et al. deduced local densities from shifts $\Delta\nu$ in the frequency of a particular Raman-active vibration of fluoroform from its gas-phase value. If the relationship between $\Delta\nu$ and (local) density, $\Delta\nu = f(\rho)$, is known, local densities are obtained by inverting this function, i.e., using the relation $\rho_{\text{local}} = f^{-1}(\Delta\nu_{\text{obs}})$. But the same experimental data set can provide very different estimates of ρ_{local} depending on the choice of the function f . Saitow et al. [14] modeled vibrational line shifts according to the theory of Schweizer and Chandler [20].

Because the repulsive contribution to the shift was predicted to be small, and because the attractive component of the shift was assumed to result from dispersive forces and be simply proportional to solvent density, their treatment is essentially equivalent to postulating $\Delta\nu = c\rho_{\text{local}}$, i.e., $f(\rho) = c\rho$, where c is a constant. Although this choice is reasonable, other dependencies are equally plausible.

For example, vibrational line shifts have often been interpreted using dielectric continuum models of solvation [21,22], in much the same way as have electronic spectral shifts [23]. Depending on whether the mode in question is assumed to be predominantly affected by polar or nonpolar interactions, such approaches predict vibrational frequency shifts to be proportional to some function of dielectric parameters. In the case of nonpolar coupling one expects $\Delta\nu = cF(n^2)$ whereas if polar interactions are of most importance $\Delta\nu = c\{F(\epsilon) - F(n^2)\}$, where F describes how the reaction field acting on the solute depends on the solvent dielectric parameters n (refractive index) and ϵ (dielectric constant). Different theories predict a variety of functional forms for F [24]. Two common choices that illustrate the range of behaviors expected are $F_1(x) \equiv (x-1)/(x+2)$ and $F_2(x) \equiv (x-1)/(2x+1)$ [25]. The density dependence of $\Delta\nu$ is implicit in the dependence of the dielectric parameters on solvent density, assumed to be known empirically. As discussed previously with respect to electronic shifts [3], in the case of polar fluids, these various possibilities give rise to very different predictions for local densities.

This fact is illustrated in Fig. 3, where we plot the normalized density dependence of these dielectric functions using parameterizations of experimental dielectric data for fluoroform [3]. For comparison, normalized values of the vibrational frequency shifts observed in experiment (points) are also plotted. The bottom panel of Fig. 3 illustrates the density dependence expected if the vibrational shifts are sensitive only to the electronic polarizability of the solvent, represented by the dielectric functions $F_1(n^2)$ and $F_2(n^2)$. In this case, either choice of nonpolar reaction field predicts that $\Delta\nu$ should be nearly proportional to bulk density. If one interprets the observed shifts in this

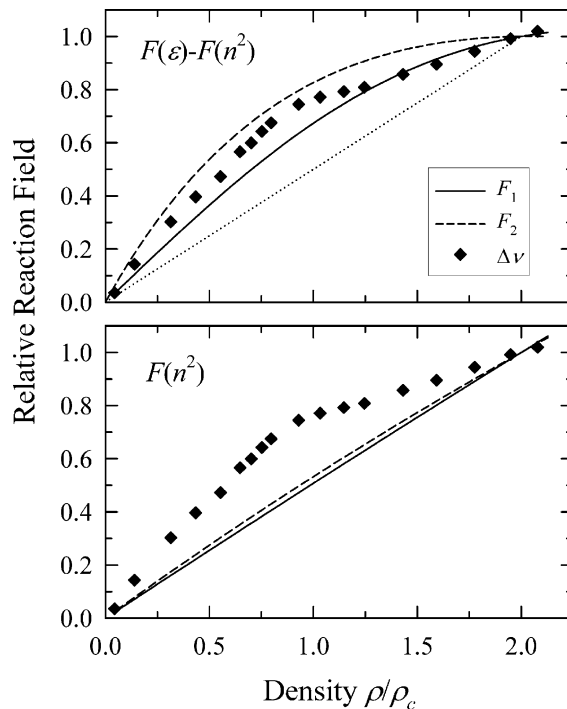


Fig. 3. Density dependence of the nuclear or polar reaction field $F(\epsilon) - F(n^2)$ and the electronic or nonpolar reaction field $F(n^2)$. Values are normalized to unity at the reference density $2\rho_c$. In each case, values using two alternative reaction fields are shown, $F_1(x) = (x-1)/(x+2)$ (solid curves) and $F_2(x) = (x-1)/(2x+1)$ (dashed curves). Also shown are the normalized values of the observed Raman shift ($\Delta\nu$) of the symmetric CF_3 stretch of fluoroform (points; [15]).

manner, the much larger nonlinearity in $\Delta\nu_{\text{obs}}(\rho)$ implies large values of $\Delta\rho$, which can be read from this plot as the horizontal distance between $\Delta\nu_{\text{obs}}(\rho)$ and $F_i(n^2)$. Both reaction fields imply a maximal density augmentation of $\Delta\rho_{\text{max}}$ of $\sim 0.5\rho_c$, i.e., the result reported by Saitow et al. [14]. If instead, one assumes that the vibrational shifts respond to the ‘nuclear’ polarizability of the solvent, i.e., the response coming from the permanent charge distributions of solvent molecules, the relevant reaction field functions are the $F(\epsilon) - F(n^2)$ shown in the top panel of Fig. 3. In contrast to $F_i(n^2)$, the collective nature of the dielectric response in polar fluids renders this latter reaction field a highly nonlinear function of bulk density. Assuming $\Delta\nu \propto F(\epsilon) - F(n^2)$ one would therefore infer the presence of a much smaller density aug-

mentation. Using the reaction field F_1 , a maximal density augmentation of $\Delta\rho_{\max} \sim 0.2\rho_c$ is obtained, comparable to what was found from the simulations of the previous section. If the alternative choice of nuclear reaction field F_2 is used, rather than density augmentation, a density *depletion* is implied. Thus, depending on whether the spectral shift is believed to be sensitive to the electronic or nuclear polarizability of the solvent, and depending on which dielectric formulation one chooses in the latter case, quite different conclusions are reached concerning the nature of local densities in polar fluids such as fluoroform.

On the basis of these observations, we conjecture that the much larger density augmentation reported for fluoroform compared to other neat supercritical fluids probably results in part from incorrect assumptions made about the origins of the vibrational shifts observed. As will be discussed in more detail later, it is reasonable to expect that polar interactions contribute significantly (or even dominate) the spectral shifts of the symmetric CF_3 stretch of fluoroform. If so, the extent of augmentation implied by the observed shifts would be much smaller than originally reported, and more in keeping with previous results.

4. Perspectives from simulation

Additional insight into the different density dependences of polar versus nonpolar observables is provided by the further analysis of the fluoroform simulations displayed in Fig. 4. In this figure the Lennard-Jones and electrical components of the interaction energy (circles) and bond force (triangles), the net force on the pseudo-diatomic bond, are shown ratioed to either the bulk solvent density (Fig. 4a) or to the 1st shell coordination number (Fig. 4b). These data have also been normalized to their values at the reference density $2\rho_c$ to facilitate comparison (un-normalized values are provided in Table 1). Fig. 4a illustrates the fact that none of these observables are simply proportional to bulk density, although the Lennard-Jones contribution to the energy is nearly so. Departure from unity in this representation is due both to intrinsic nonlinearity in the quantity's density dependence and to

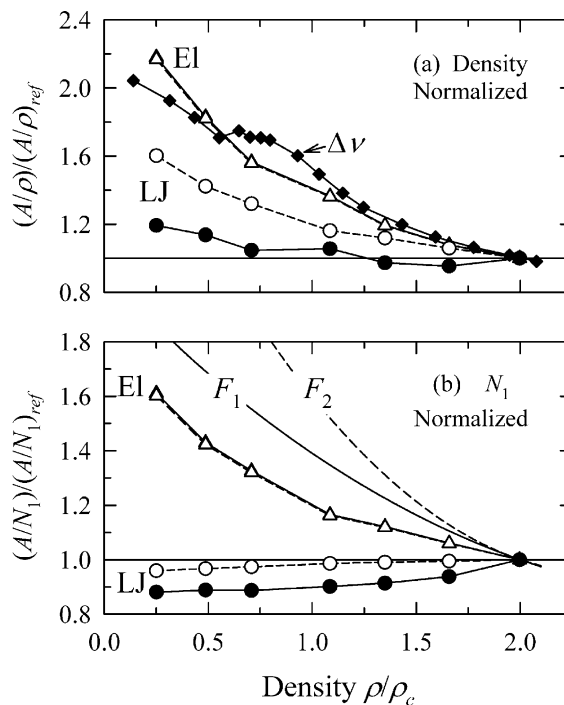


Fig. 4. Density-normalized observables 'A' simulated for neat fluoroform. In panel (a) observables are normalized to the bulk solvent density, whereas in panel (b) they are normalized to the 1st shell coordination number N_1 . To facilitate comparison, each observable has been further normalized to its value at a reference density of $2\rho_c$. The quantities plotted are the Lennard-Jones (open circles) and electrical (open triangles) components of the interaction energy and the Lennard-Jones (filled circles) and electrical (filled triangles) components of the bond force. (The electrical energies and bond forces are nearly indistinguishable in this figure.) Panel (a) also contains the observed Raman shifts (Δv ; filled diamonds) of the symmetric CF_3 stretch of fluoroform ([15]). The smooth curves in panel (b) labeled ' F_1 ' and ' F_2 ' are N_1 -normalized values of the nuclear reaction field factors $F_1(\epsilon) - F_1(n^2)$ and $F_2(\epsilon) - F_2(n^2)$.

the effects of density augmentation. The electrical contributions to the energy and bond force (indistinguishable in this figure) show the largest departures from a simple proportionality to density, as anticipated from the dielectric continuum analysis just presented. Also plotted in Fig. 4a are density-normalized values of the Raman shifts observed by Saitow et al. (diamonds) [14]. In first approximation, the shift of a vibrational line should be proportional to the projection of the force on the normal coordinate, which is simply the bond force

in the diatomic representation of fluoroform employed here. The fact that the experimental shifts track the electrical component of the simulated bond force again suggests that the observed shifts may be better explained as being due to electrical (polar) interactions.

Fig. 4b shows the energy and force components normalized to the 1st solvation shell coordination numbers N_1 . In this representation an observable that is a direct measure of 1st solvation shell densities would be unity at all bulk densities. As has been noted in previous simulations of polyatomic solutes [6], the Lennard-Jones component of the solvation energy (open circles) tracks the 1st shell density with high fidelity over the entire density range. The Lennard-Jones contribution to the bond force differs from unity by only about 10%, so that it too provides a nearly direct measure of local density in this system. However, consistent with the dielectric continuum analysis, electrical contributions to the solvation energy and bond force are not simply proportional to bulk densities. Correlations between the orientations of neighboring molecules render the electrical solvation energy and force are highly nonlinear function of coordination number or local density. Qualitatively speaking, the values of $(F_{\text{el}}/N_1)_{\text{rel}} \sim 1.6$ at the lowest density simulated indicate that the presence of an additional solvent molecule in the 1st solvation shell has a 60% greater effect on the electrical interactions at low densities compared to high densities. As already discussed with respect to Fig. 3, if one ignores this nonlinearity and assumes a proportionality to density for an observable that is significantly influenced by polar interactions, the extent of density augmentation will be exaggerated. We believe that this is the case with the vibrational shifts of fluoroform.

Of course, even when an observable is dominated by polar solvent interactions, it can still be used to measure local densities, as long as its dependence on density is understood. Because dielectric continuum estimates are usually used for this purpose, it is interesting to compare dielectric predictions to these simulation results. The two smooth curves in Fig. 4b show the normalized density dependence of the two polar reaction field functions discussed previously, $F_1(\varepsilon) - F_1(n^2)$ and

$F_2(\varepsilon) - F_2(n^2)$. We note that both functions significantly overestimate the nonlinearity in the density dependence of the electrical solvation energy and bond force [26]. As suggested previously from experimental evidence [3], the F_1 reaction field is the better choice, but it still overestimates the values at low density by 15–20%. Estimates of electrical solvation energies based on molecular models [27] are probably required for greater accuracy.

5. Origins of the vibrational shift

The previous sections suggest that a more satisfying interpretation of the Raman data of Saitow et al. would result by assuming that these shifts are primarily sensitive to dipolar rather than dispersion interactions. We finally examine whether such an assumption is reasonable using two approaches. First we consider the simulation results. According to standard theory [28] the solvent-induced shift of a vibrational band can be described in terms of an expansion in the vibrational coordinate Q whose lowest-order term is [29]

$$\hbar\Delta\omega \cong [Q_{11} - Q_{00}] \overline{\left(\frac{\partial V}{\partial Q}\right)}_{Q=0} + \dots$$

$$\text{with } [Q_{11} - Q_{00}] = \frac{-\hbar f}{2m^{3/2}\omega_0^3}. \quad (2)$$

In this expression ω_0 , m , and f are the harmonic frequency, the reduced mass, and the cubic anharmonicity constant of the vibration and $V = V(\vec{R}_{0j}, \mu)$ is the solute–solvent interaction potential, which is a function of the relative solvent–solute coordinates \vec{R}_{0j} and the solute dipole moment μ . The overbar on $\overline{(\partial V/\partial Q)}_{Q=0}$ indicates ensemble averaging over solvent coordinates. For the diatomic representation of fluoroform used here this derivative can be expressed

$$\left(\frac{\partial V}{\partial Q}\right)_{Q=0} = \left[\left(\frac{\partial V}{\partial \vec{R}_{0j}}\right) \left(\frac{\partial \vec{R}_{0j}}{\partial Q}\right) + \left(\frac{\partial V}{\partial \mu}\right) \left(\frac{\partial \mu}{\partial Q}\right) \right]_{Q=0}$$

$$= -\bar{F} - \bar{E} \left(\frac{\partial \mu}{\partial Q}\right)_{Q=0} \cong -\bar{F} + \frac{\bar{U}_{\text{el}}}{\mu} \left(\frac{\partial \mu}{\partial Q}\right)_{Q=0}, \quad (3)$$

where \bar{F} denotes the average force on the vibration (the bond force here) and \bar{E} is the average electric field on the bond, which should be well approximated by the electrical component of the solvation energy collected in simulation. The last relation above shows that the vibrational shift can be separated into contributions from Lennard-Jones (i.e., repulsion–dispersion) and electrical forces

$$\begin{aligned} \left(\frac{\Delta\nu}{\nu_0}\right)_{\text{LJ}} &\cong a\bar{F}_{\text{LJ}} \text{ and} \\ \left(\frac{\Delta\nu}{\nu_0}\right)_{\text{El}} &\cong a\left\{\bar{F}_{\text{El}} - \frac{\bar{U}_{\text{el}}}{\mu}\left(\frac{\partial\mu}{\partial Q}\right)_{Q=0}\right\}, \end{aligned} \quad (4)$$

where $a = f/(2\mu^{3/2}\omega_0^4)$ and $\nu_0 = \omega_0/2\pi$.

To determine the molecular constants needed for evaluating Eq. (4) we performed ab initio calculations at the MP2/6-311G(d) level using the GAUSSIAN 98 program [30]. These calculations yielded the values: $\mu = 1.88$ D (expt. = 1.65 D [31]), $\bar{\nu}_0 = 1165$ cm^{-1} (expt. = 1136 cm^{-1} [14]), $f = -1.0 \times 10^{13}$ N m^{-2} , and $(\partial\mu/\partial Q)_{Q=0} = 5.3$ D/\AA for the symmetric CF_3 stretch. Using the results in Table 1, for a density of $2\rho_c$, we find $\Delta\bar{\nu}_{\text{LJ}} = +0.9$ cm^{-1} and $\Delta\bar{\nu}_{\text{El}} = -6.2$ cm^{-1} . Thus, this calculation predicts that electrical interactions should dominate the total shift. Compared to the experimental shift of $\Delta\bar{\nu} = -19.2$ cm^{-1} , the predicted shift is too small by a factor of ~ 3 . However, better agreement is not expected given the facts that we have ignored the second-order terms in Eq. (2) and that the diatomic model of fluoroform used here provides only a crude representation of the real molecular shape. More detailed analysis on an all-atom model of fluoroform would be expected to yield better quantitative agreement with experiment. Nevertheless, these calculations strongly suggest that electrical interactions are primarily responsible for the observed shifts.

Further support for this claim is provided by an alternative estimate of the solvent effect on the vibrational shift. We have repeated the ab initio calculations of fluoroform described above using a self-consistent reaction field approach. Using the self-consistent isodensity polarized continuum ‘SCI-PCM’ method [32], which incorporates a realistic representation of the molecular shape [33] we calculated frequency shifts at $2\rho_c$ assuming: (i)

only the solvent electronic polarizability ($\epsilon = n^2 = 1.35$) and (ii) the full dielectric response of the solvent ($\epsilon = 8.1$, $n^2 = 1.35$). The two calculations yield frequencies differing from the gas phase value by $\Delta\bar{\nu} = -5$ and -25 cm^{-1} , respectively. Interpreting the difference between these two calculations as reflecting the effects of permanent electrical charges of the solvent, these results again point to electrical interactions dominating the solvent effect on the symmetric CF_3 stretch. We note that in this case, the shift of -25 cm^{-1} predicted by calculation (ii) is quite close to the experimental value of -19.2 cm^{-1} . But given the uncertain isodensity boundary value required [33] as well as the neglect of repulsive effects, this level of agreement must be considered largely fortuitous.

6. Summary and conclusions

We have used computer simulations and dielectric analyses to explore the differences between local density augmentation and its experimental determination in neat polar and nonpolar supercritical fluids. This work was prompted by a recent Raman investigation by Saitow et al. [14] who reported unexpectedly large local densities in neat fluoroform near the critical point and suggested that electrical interactions might be the source of this large effect. We simulated the solvation structure of simplified models of fluoroform and ethane as functions of density on an isotherm slightly above T_c . The simulations point to increased augmentation in fluoroform compared to ethane as a result of the electrical interactions present in the former solvent. However, the extent of the density augmentation simulated in both systems is modest ($\Delta\rho_{\text{max}} = 0.12$ and $0.15\rho_c$), in keeping with expectations from prior studies, but much smaller than reported by Saitow et al. ($\Delta\rho_{\text{max}} \cong 0.5\rho_c$). We suggest that the reason for this discrepancy relates to how local densities are derived from the Raman data. Saitow et al. assumed that the solvent-induced shifts of the symmetric CF_3 stretch of fluoroform result from nonpolar interactions of the vibration with its surroundings. Both dielectric continuum theories

and simulation results indicate that if the interactions are instead modeled as being primarily electrical in character, the local densities inferred from the experimental data are much smaller than reported in [14] and close to the values simulated in fluoroform. Preliminary analyses using characteristics of the symmetric CF_3 stretch calculated via ab initio methods suggest that such a reinterpretation of the data is justified.

The results of the present work reinforce previous observations [3] concerning ambiguities that arise when determining local densities in polar systems. In *nonpolar fluids* many solute-centered observables can be safely assumed to be proportional to local density. The reason is that both repulsive and attractive interactions involving the solvent's electronic polarizability are nearly proportional to local density. However, in *polar fluids*, when the nuclear polarizability (permanent charge response) of the solvent is important to the observable of interest, this simple connection is no longer valid. The collective nature of polar interactions renders the relationship between local density and observables such as spectral shifts highly nonlinear. Although dielectric continuum models of the sort employed in Section 3 provide some guidance, remaining uncertainties in this relationship necessarily lead to significant uncertainties in the local densities deduced from experiments in polar fluids.

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Appendix A. Simulation details

The fluoroform model employed for simulations was the 2-site Lennard-Jones plus Coulomb representation parameterized by Song et al. [15]. The parameters of this model are: $\epsilon/k_B = 85.48$ K, $\sigma = 3.50$ Å, $q = \pm 0.275e$, $m = 35.01$ amu, and $L = 1.67$ Å (the Lennard-Jones well depth and size

parameters, site charge, mass, and bond length, respectively.) The ethane model was the 2-site 'TraPPE' potential of Martin and Seipmann [16], which uses the parameters $\epsilon/k_B = 98$ K, $\sigma = 3.75$ Å, $m = 15.035$, and $L = 1.54$ Å. Simulations were performed on 1000-molecule samples in the (*NPT*) ensemble using a modified version of the DL_POLY program [34]. The Hoover algorithm was used for maintaining constant temperature and pressure with thermostat and barostat time constants of 1 ps. A time step of 2 fs and cubic periodic boundary conditions were used for both fluids. In the case of ethane, intermolecular interactions were truncated at a cutoff distance of 14 Å. In the case of fluoroform a 12 Å cutoff was used for the Lennard-Jones interactions and whereas the electrical interactions were treated using an Ewald summation. Simulations were carried out for 1 ns starting from configurations that had been previously equilibrated for at least 1 ns.

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