

Reply to “Comment on ‘Behavior of Supercritical Fluids across the Frenkel Line’”

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In a recent Letter,¹ we scrutinized structural and dynamical properties of a supercritical fluid in connection with the “Frenkel line” (FL) concept.² In particular, we discussed the existence of a low-frequency cutoff for transverse modes and the disappearance of the medium-range order across the FL, as well as the expression for the positive sound dispersion and specific heat within the FL approach.

The Comment by Brazhkin et al.³ starts with an introduction questioning the robustness of the Widom line against the FL as a demarcation of different regions in the supercritical state, reminiscent of subcritical behavior. This is the leitmotif of a querelle initiated by Brazhkin et al. back in 2012,² six years after our first paper on the experimental demonstration for the existence of gas-like and liquid-like regions in the supercritical phase.⁴ Brazhkin et al. build on the obvious, recalling that “the Widom line exists only in the vicinity of the critical point”. Less obvious is why they arbitrarily decide that a line “cannot be extrapolated into the range of experimental interest”. Further, Brazhkin et al. claim that (we) “have subsequently realized their mistake when they found the dynamical crossover in the soft-sphere system⁵ and hard-sphere system⁶ where the critical point and thermodynamic anomalies do not exist”. It is easy to check that in refs 5 and 6 we neither realize any mistake nor recant anything of our original findings. In their misrepresentation, Brazhkin et al. are apparently not aware that we repeatedly stressed (see for instance ref 7) how the locus of heat capacity maxima, originally introduced in the argon case,⁸ is just one possible choice to represent the Widom line, which is more generally defined by the maxima of correlation length in the vicinity of the critical point. We clearly demonstrated how the entire picture of the gas-like and liquid-like region parted by the Widom line is valid using different observables such as thermal diffusivity or kinematic viscosity as relevant correlation lengths.⁷ Hence, refs 5 and 6 consolidate our initial findings,⁸ at odds with Brazhkin et al.’s misinterpretation.

Further on, Brazhkin et al. claim that we made in ref 1 “unphysical proposals such as using the infinite-frequency shear modulus to ascertain collective modes in liquids”. In doing that, Brazhkin et al. are ignoring the *exact* sum rules in collective dynamics of liquids. The second frequency moment of longitudinal (L) or transverse (T) current spectral function

$C^{L/T}(k, \omega)$ is indeed expressed via k -dependent infinite-frequency bulk $B_\infty(k)$ and shear $G_\infty(k)$ moduli.^{10,13} Namely, these quantities appear in the solution of the generalized Langevin equation for L and T time correlation functions outside the hydrodynamic regime, as the L/T “bare frequencies” (nondamped oscillators) which, due to memory effects, are renormalized to the observed L/T dispersion $\omega_{L/T}(k)$ of collective excitations.^{10,21} Accordingly, neither “incorrect conclusions are drawn” nor “grossly skewed picture emerges and misleads readers” from our Letter.¹

Below we reply to the five issues addressed in the Comment point-by-point.

■ POINT 1

The static structure factor, $S(k)$, and the pair distribution function, $g(r)$, encode the same information in different forms, being essentially related by a Fourier transform. No result can depend on the domain of choice. We originally showed $g(r)$ just because this is the most direct way to address particle correlations from molecular dynamics (MD), which is the technique used in our paper, while scattering experiments can directly access only $S(k)$.

Evaluating $S(k)$ from $g(r)$ can indeed introduce critical mistakes, especially if this is done using expressions which are subject to significant numerical errors (see for example eq 1 of ref 9). In this Reply we evaluated $S(k)$ from MD simulations (the setup of simulations with 4000 particles modeling supercritical Ne is the same as in ref 1) in the most accurate way, i.e., directly from the k -domain static density–density correlation $S(k) = \langle n(-\mathbf{k})n(\mathbf{k}) \rangle$. Averages were performed for over 60 000 configurations and with all possible directions of the wave vectors \mathbf{k} corresponding the same absolute value k (up to 72 different directions). The result is shown in Figure 1 and, as expected, is in line with the conclusions which we previously obtained by analysis of $g(r)$, i.e., clearly showing a smooth evolution of both the position and the maximum of the main diffraction peak vs pressure. Actually, one can apply a theory to

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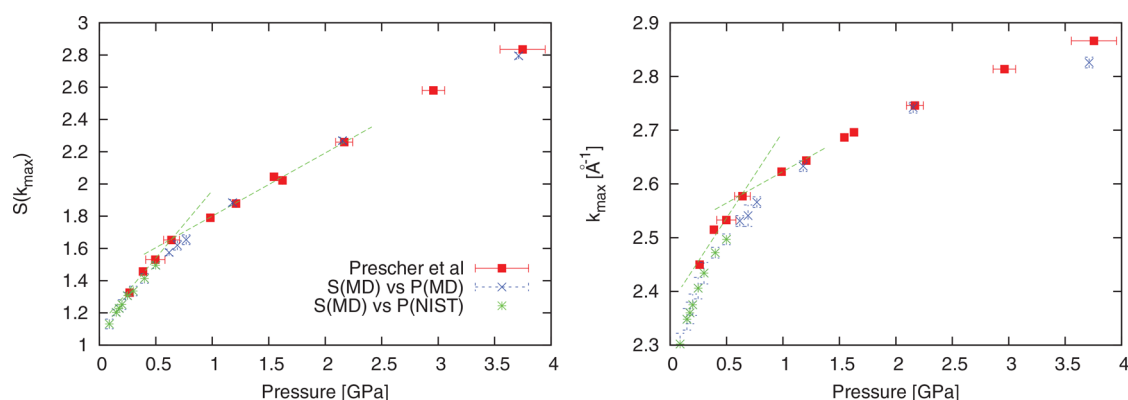


Figure 1. Comparison of experimental⁹ and MD results for main peak height of $S(k)$ and its position k_{\max} as the functions of pressure in supercritical Ne. Green asterisks show the results plotted vs those available in the NIST database¹² pressures ($P < 0.5$ GPa), which practically overlapped with our MD points. Lines correspond to linear fits from ref 9 with the purpose to highlight a possible kink in the reported pressure dependence.

resolve the issue regarding whether by crossing the “Frenkel line” the main diffraction peak location of static structure factor $S(k)$ as a function of pressure contains a kink or not. A simplest case of the Percus–Yevick approximation for hard-sphere fluids¹⁰ shows the smooth pressure dependence of the k_{\max} of $S(k)$ too (see Figure 2). According to MD simulations of

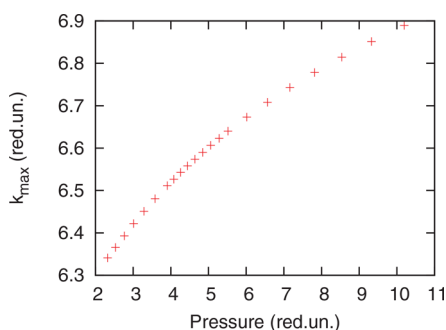


Figure 2. Location of the main diffraction peak for hard-sphere fluids as a function of pressure, obtained from Percus–Yevick theory.¹⁰ All quantities are in reduced units generally adopted for hard spheres.

transverse modes in hard-sphere fluids⁶ the disappearance of shear waves from the spectrum of transverse excitations takes place in the range of packing fractions, η , 0.37–0.395. This range of packing fractions corresponds to pressure range $P \sim 4.26$ – 5.88 , and as one can see from Figure 2, the Percus–Yevick theory of $S(k)$ for hard-sphere fluids does not show any kink in the pressure dependence of the main diffraction peak position. Similar results for realistic supercritical fluids for $S(k)$ obtained by integral equation theory will be published elsewhere.

Brazhkin et al. raise ethical issues against the authors in ascribing to us incorrect statements about the disappearance of the medium-range order (3rd maximum of $g(r)$) across the “Frenkel line”. In our paper we merely stressed the absence of abrupt changes in medium-range order, and we are happy if Brazhkin et al. are in line with the same conclusion in some of their statements. However, this is certainly contradicted by the sentences in their papers:¹¹ “experimental results, supported by extensive molecular dynamics simulations, show disappearance of the medium-range order” and in ref 9 “our experimental data suggests a constant third peak height in the gaslike region indicating loss of medium range order across the Frenkel line”.

POINT 2

The statement by Brazhkin et al. “Below the FL where transverse modes operate, the longitudinal sound velocity acquires a well-known value $v = \sqrt{\frac{B + \frac{4}{3}G}{\rho}}$, where B and G correspond to their high-frequency values¹³” is not correct. There is no such expression for the longitudinal sound velocity in ref 13 and cannot be. The macroscopic longitudinal speed of sound is the hydrodynamic adiabatic one, $v \equiv c_s$. If Brazhkin et al. meant the *apparent* longitudinal speed of propagation of acoustic-like excitations outside the hydrodynamic regime $v(k) = \omega_L(k)/k$, they had to use some analytical dispersion law $\omega_L(k)$, which is in general unknown for liquids in the high-frequency regime. At the boundary of the hydrodynamic regime, the dispersion law can be represented by the analytical solution of the thermo-viscoelastic model.¹⁴ However, as for the dispersion in the high-frequency regime, in some approximation (for k -values far outside the hydrodynamic regime) and in the neglect of coupling to nonhydrodynamic excitations, it approximately reads

$$\omega_L(k) \approx \sqrt{\left[B_\infty(k) + \frac{4}{3}G_\infty(k) \right] k^2 / \rho - \sigma_L^2(k)} \quad (1)$$

with k -dependent high-frequency bulk $B_\infty(k)$ and shear $G_\infty(k)$ moduli (see the definitions 2.4.20, 2.4.23, and 2.4.24 in ref 13), with ρ being mass density, and $\sigma_L(k)$ being the damping of longitudinal excitations, which cannot be neglected. Hence, the explanation of the positive sound dispersion given by Brazhkin et al. is critically undermined by a wrong starting point.

We now address the sentence by Brazhkin et al.: “However, Bryk et al. choose not to mention that we have in fact calculated the high-frequency B and found it not too different from the static value of B at high density¹⁵”. This is certainly not true: in Figure 4 of the commented Letter,¹ we reported the static B_0 and the high-frequency B_∞ moduli, exactly calculated by definitions.¹⁵ The latter exceeds by a factor of 2 the former over the entire density range, so the quantitative difference between those two (qualitatively completely different) quantities is certainly not negligible. On passing, we note that in ref 15 the only information supplied is that $B(\omega) \approx B(0)$ without any numbers or explanations on how $B(\omega)$ was calculated and relates to the infinite-frequency modulus $B_\infty = B_\infty(k \rightarrow 0)$.

The following discussion on positive sound dispersion and high-frequency elastic moduli by Brazhkin et al. contains an

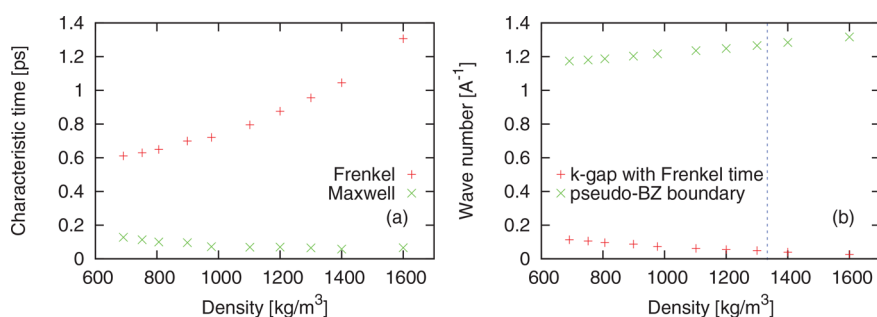


Figure 3. Frenkel jump τ_F and Maxwell relaxation τ_M times, calculated from MD simulations of supercritical Ne¹ for different densities (a) and comparison of the values of the first pseudo-Brillouin zone boundary with the k -gap estimated via the Frenkel time τ_F (b). The dashed vertical line in (b) corresponds to the location of FL, at which according to Brazhkin et al. the k -gap has to reach the first pseudo-Brillouin zone boundary.

important conceptual mistake on the correct definition of the elastic regime in liquids and on the relation between the elastic moduli and the dispersion of corresponding excitations. The text “the excitation spectrum of a fluid at high temperature or low pressure does not include transverse frequencies. This is witnessed by the data in Figure 3 in Bryk et al.’s paper,¹ implying that that the high-frequency shear modulus is zero as expected” indicates that Brazhkin et al. identify transverse excitation frequencies observed in MD simulations directly with the shear modulus, and that is not correct due to damping effects. The frequencies of transverse excitations are

$$\omega_T(k) = \sqrt{G_\infty(k)k^2/\rho - \sigma_T^2(k)} \quad (2)$$

where $\sigma_T(k)$ represents the damping of the transverse modes. If the damping $\sigma_T(k)$ is strong enough, the transverse excitations cannot propagate even having nonzero shear modulus $G_\infty(k)$. Actually, the emergence of the propagation gap for long-wavelength transverse excitations is defined by the strong damping due to Maxwell relaxation.

POINT 3

With respect to our result in ref 1 on the evidence for existence of transverse excitations below ω_F , Brazhkin et al. claim that we are giving a “misinterpretation” as they “have not used the criterion $\omega = \omega_D$ as a condition for disappearance of transverse modes”. This is in striking contradiction with the original paper by Brazhkin et al. on FL,² which reads “solid-like shear waves exist in the range of $2\pi/\tau_F < \omega < 2\pi/\tau_D$ ”, where τ_D is the “minimal (Debye) vibration period”, which would imply that transverse excitations disappear when the two bounds coincide, i.e., when ω_F reaches ω_D . The recent paper by Brazhkin¹⁶ reads indeed “...the above argument predicts that liquids are capable of supporting shear waves, the property hitherto attributable to solids only, but only for frequencies above ω_F ”. The commented Letter simply demonstrated that ω_F does not represent at all such a lower-frequency bound for the propagation of transverse waves (Figure 3a in ref 1).

Brazhkin et al. in ref 3 do not show explicit subindices for their τ ; therefore, it is critical to remind the readers that the k -gap for T-excitations is defined by the Maxwell relaxation time τ_M ,^{10,17,18} which reflects the macroscopic shear stress relaxation, and which can be generalized to microscopic scales using k -dependent shear viscosity $\eta(k)$ and $G_\infty(k)$. Note that $\tau_M(k)$ is a collective property and cannot be reduced to the single-particle “Frenkel jump time” τ_F , which Brazhkin et al. use in the expression for the k -gap. In Figure 3a, we show, calculated from MD simulations, single-particle Frenkel time and collective

Maxwell relaxation time and the large difference between them. The Stokes–Einstein (SE) ratio, which involves the self-diffusion coefficient D , shear viscosity η , and particle size a can be naturally used to make some estimates regarding how different Frenkel time and Maxwell relaxation time are. A simple application of the SE ratio to τ_F/τ_M leads to

$$\frac{\tau_F}{\tau_M} = \frac{a^2 G_\infty}{6D\eta} \stackrel{\text{apply SE}}{=} \frac{\pi a^3 G_\infty}{2k_B T}$$

which is more than a factor 20 for $T = 295$ K, density 1600 kg/m³, $a \sim 2.7$ Å, and $G_\infty \sim 3.4$ GPa and is in agreement with what is observed in Figure 3a, difference between the microscopic Frenkel and macroscopic Maxwell times.

POINT 4

As for the most appropriate estimation of the FL, the two “quantitative criteria” mentioned by Brazhkin et al. are both subject to serious problems.

The specific heat approach (FL estimation via $C_V = 2k_B$) has been obtained using an untenable approximation for liquids, based on nondamped acoustic modes. The sentence “Bryk et al. incorrectly apply this result to the hard-spheres system,⁶ the system known to be strongly anharmonic” is a sneaky way to admit, turning around the tables, that the condition $C_V = 2k_B$ does not possess the key ingredient of any definition, i.e., generality. In our Letter¹ we simply highlighted this problem.

As for the estimation of the FL via the velocity autocorrelation function (VACF), this is based on the identification of a transition from an oscillatory behavior to a monotonically decaying function, a highly arbitrary criterion without any connection with the original FL $\tau_F = \tau_D$ definition.² Furthermore, recent detailed theoretical and simulation analysis of contributions from collective modes to VACF¹⁹ shows that at densities far above the FL there exist nonvanishing oscillating contributions.

POINT 5

Brazhkin et al. raised an issue of the propagation gap for transverse excitations in liquids and how this gap is mirrored in the specific heat. Beside a “technical” point on a typographical mistake,²⁰ this is a lengthy discussion in order to justify nonexistent low-frequency cutoff for transverse excitations ω_F . The emphasis given by the authors of the Comment on the justification of the low-frequency integration bound ω_F in their eq 1 diverts away from the real problem. On a more physical ground, the Comment again misses the point already discussed

in our reply to issue 3: the expression for the transverse excitations k -gap^{17,18}

$$k_g = \left[\frac{\rho G_\infty(k)}{4\eta^2(k)} \right]_{k \rightarrow 0}^{1/2} = \left[\frac{\rho G_\infty}{4\eta^2} \right]^{1/2} \equiv \frac{1}{2c_T \tau_M} \quad (3)$$

is defined by the Maxwell relaxation time $\tau_M = \eta/G_\infty$, and transverse speed of “bare” (nondamped) transverse excitations $c_T^2 = G_\infty/\rho$. The use of the Frenkel time in the lower bound of the integrals (eqs 1, 2, and 4 of the Comment) is conceptually wrong. In Figure 3b we show the values for the k -gap if the Frenkel time in the right-hand side of eq 3 was used, as claimed by Brazhkin et al. Due to a large difference in τ_M and τ_F , the k -gap originating from Frenkel mechanism is too small and will not reach the pseudo-Brillouin zone boundary at the “Frenkel line”, i.e., contrary to that predicted by Brazhkin et al.³ In Figure 3b the first pseudo-Brillouin zone boundary at different densities was calculated in the standard way as a half of the k -location of the main diffraction peak of $S(k)$. The vertical dashed line indicates the “Frenkel line” location for the studied isothermal line of supercritical Ne and shows disagreement with the claim by the Brazhkin et al. merger of the k -gap due to Frenkel jumps with the first pseudo-Brillouin zone boundary at FL, eq 2 of the Comment. The correct theory^{10,17,18} of the k -gap with Maxwell relaxation time (eq 3) and results shown in Figure 3 provide evidence that the Frenkel jumps cannot be connected with the gap for nonhydrodynamic transverse excitations in fluids.

There are also some minor points we would like to reply to: (a) The purpose of that reference is to acknowledge the work of Benjamin Widom, who first pointed out odd fluctuations in fluids near the critical point. Obviously the line has not been named after by Widom himself. (b) In ref 22 where, at variance with what erroneously reported in the present Comment, nowhere was the claim that the “change of dynamics was observed at $(0.7-0.8)T_c$ ”. On the contrary, the data in Figure 3 of ref 22 clearly show the dynamical crossover taking place at T_c as expected.

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Notes

The authors declare no competing financial interest.

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(20) As for the power index “2” missing in shear viscosity of eq 24 of the 2011 paper,²¹ which according to Brazhkin et al. would prevent the possibility of using that result: this is clearly a typographical mistake which we already spotted (an Erratum on eq 24 of ref 21 has been published, see DOI 10.1140/epjst/e2018-80002-0) and in no way it hampers the validity of our conclusions. All of the following expressions for the relaxing eigenmodes (eq 25) as well as dispersion $\omega_T(k)$ and damping $\sigma_T(k)$ of shear waves (eq 26) are indeed correct.

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