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Comment

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Comment on "Behavior of Supercritical Fluids across the Frenkel Line"

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The Frenkel line (FL) is the line of change of particle dynamics and qualitative change of the excitation spectrum of the fluid [1–4]. The FL was used to explain important supercritical properties. This included an alternative interpretation [4] of experimental findings in Ref. [5] by Simeoni, Bryk et al originally attributed to the Widom line. As we showed [1, 3, 6–10], the Widom line exists only in the vicinity of the critical point and can not be extrapolated into the range of experimental interest. Bryk et al have subsequently realized their mistake when they found the dynamical crossover in the soft-sphere system [11] and hard-sphere system [12] where the critical point and thermodynamic anomalies do not exist.

A recent paper by Bryk et al entirely focuses on making critical remarks about the FL [13]. On five counts, their remarks involve choosing the data and results selectively rather than discussing the data in their entirety. On three further counts, their remarks are clear misrepresentations of our discussion of the FL. In remaining instances, unphysical proposals are made such as using the infinite-frequency shear modulus to ascertain collective modes in liquids or incorrect statements are included (sometimes of secondary importance, such as advocating incorrect equations for the k-gap having wrong dimensionality). As a result, incorrect conclusions are drawn and a grossly skewed picture emerges and misleads readers. Below we address and correct the points one by one.

1. Bryk et al choose to show the pair distribution function $g(r)$ calculated in our previous paper [14] as a Fourier transform of the structure factor $S(q)$ measured in supercritical Ne, compare it with their results of molecular dynamics (MD) simulations and observe the disagreement. However, the alleged disagreement disappears once the error bars in their Fig. 2 are taken into account. Bryk et al add that the difference between the experimental and simulated $g(r)$ can be due to errors involved in the Fourier transform.

Bryk et. al choose not to discuss primary experimental data of the structure factor that involves no Fourier transform. For the benefit of the readers, we show the experimental $S(q)$ of supercritical Ne in Fig. 1. This clearly shows the crossover of the structural features at pressure corresponding to the FL [14].

In addition to Ne, we show the primary Raman scattering data of supercritical CH_4 [15] in Fig. 2. The data clearly show the crossover of the dynamical features at the conditions corresponding to the FL.

Bryk et al choose not to show the earlier MD data showing the crossover of $g(r)$ at the FL [16]. This data was obtained using very fine temperature grid and better statistics due to larger system sizes and contradicts the MD data of Bryk et al in that the crossover of $g(r)$ at the FL is clearly seen.

Bryk et al state in Ref. [14] we reported the "disappearance of medium-range order" and subsequently add that contrary to our earlier results, they do not find the crossover of the third peak of $g(r)$. This clearly misrepresent our discussion. We have explicitly stated in that reference [14]: "the error bars of the experimental results are large and the data might not be accurate enough to observe a further decrease in third peak height or slight deviations from the pressure dependence of the first two peaks in g(r). Therefore, a clear answer to whether a loss of medium range order or only a change in the pressure dependence of the peak heights occur at the FL cannot be given based on our current data."

Bryk et al conclude by saying that there are "no sudden" changes of structural features at the FL, implying that this contradicts our earlier results. Bryk et al miss the point, namely that we stated the same in our earlier theoretical [16] and experimental [14] work. Indeed, we stated that there is gradual crossover of the height and location of the first peak of the structure factor as well as coordination numbers. Therefore, Bryk et al do not criticise the FL concept but their own perception of what it is.

2. Bryk et al make two points regarding the positive sound dispersion (PSD) in the supercritical system. 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 values [18]. We used this equation to calculate PSD of supercritical systems in Ref. [2, 20]. Bryk et al choose to criticise this procedure by stating that B should correspond to high-frequency value rather than the static value. 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 density [2]. At low density or smeared phase

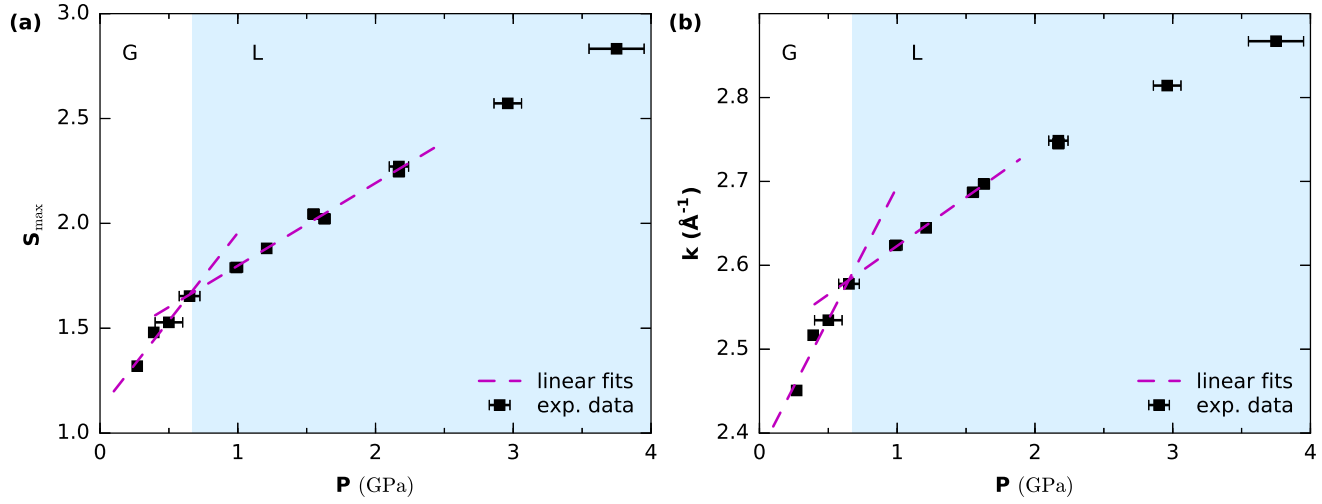

Figure 1: Height (a) and position (b) of the first maximum of the experimentally derived structure factor S(k) against pressure. The dashed magenta lines show the difference in slopes below and above the crossover. The background shadings indicate the region for gaslike (G) and liquid-like (L) supercritical fluid. From Ref. [14].

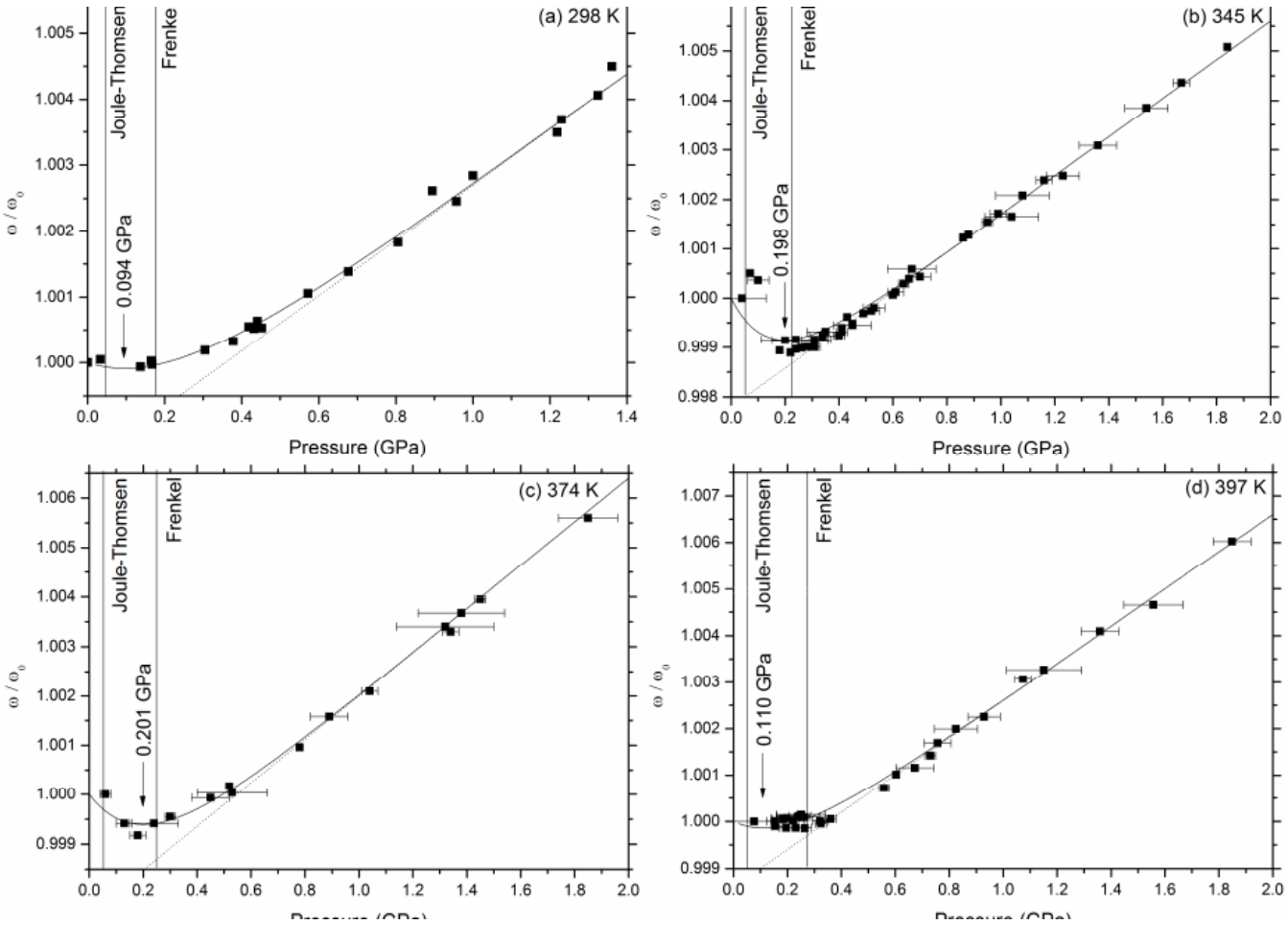

Figure 2: Plot of reduced frequency of CH4 Raman-active vibration as a function of pressure at (a) 298 K (b) 345 K (c) 374 K and (d) 397 K. Solid lines following the data are fits performed using equation (6) and arrows signify the minimum of this fit. Dotted lines are linear fits to data collected above 0.6 GPa (equation (5)). Vertical solid lines are expected positions of the Joule-Thomson line and Frenkel line. From Ref. [15].

transformations high-frequency and static B are known to differ, affecting PSD (see, e.g., [17]).

Second, Bryk et al discuss B_∞ and G_∞ in their Fig. 4 but they fail to state an important difference between high-frequency moduli and their truly infinite limits. Indeed, the infinite-frequency shear modulus of a fluid is non-zero at any low density due to the presence of the kinetic term. At the same time, the excitation spectrum of a fluid at high temperature or low pressure does not include transverse frequencies. This is witnessed by the data in Fig.3 in Bryk et al paper [13], implying that that the high-frequency shear modulus is zero as expected. The point here is that the discussion of the infinite-frequency moduli is irrelevant as far as the FL is concerned.

Once the discussion correctly addresses high-frequency, rather than infinite, shear moduli, the results of Bryk et al confirm the FL picture. Indeed, transverse modes are predicted to be present and absent below and above the FL, respectively. Bryk et al confirm this: their Fig. 3a,b show that transverse modes, non-zero high-frequency shear modulus and PSD all exist below the FL, whereas Fig. 3c,d show that the above properties disappear above the FL. This is exactly the effect of the FL that we discussed.

In passing, we note that the longitudinal sound velocity $v = \sqrt{\frac{B+\frac{4}{3}G}{\rho}}$ is not "empirical" as characterized by Bryk et al. Instead, this is a rigorous result from the elasticity theory which has been used to rationalize sound velocities in liquids both experimentally [19] and theoretically [18]). The same idea was used to interpret experimental results for viscous liquids [21] for many decades.

3. Bryk et al state that (a) $\omega = \frac{1}{\tau}$ can not be used to make a difference between the system with and without transverse modes because the gap is in k-space rather than in frequency and, consequently, (b) the equality $\omega = \omega_{\rm D}$ (ascribed to our criterion in Ref. [1, 3]) does not describe the disappearance of transverse modes.

Statement (b) is a clear misrepresentation of our discussion: we have not used the criterion $\omega = \omega_{\rm D}$ as a condition for disappearance of transverse modes. We have clearly stated (see Eq. (1) in Ref. [3]) that the condition is $\tau \approx \tau_{\rm D}$. Recalling this condition properly, statement (a) by Bryk et al becomes incorrect. Indeed, let us consider the dispersion relationship giving the gap in k-space: $\omega = \sqrt{c^2k^2 - \frac{1}{\tau^2}}$ [18, 22]. When τ starts approaching its limiting value $\tau_{\rm D}$, this dispersion law predicts that transverse modes start from zero when $k = \frac{1}{c\tau_{\rm D}} \approx \frac{1}{a}$, where a is interatomic separation, corresponding to the shortest wavelength available in the system. Therefore, all transverse modes disappear when $\tau \approx \tau_{\rm D}$, which is exactly the condition for separating the system with and without transverse modes.

In other words, the condition $\tau = \tau_{\rm D}$ can be used to demarcate the presence/absence of transverse modes in both the Frenkel picture with the frequency gap and using the dispersion law with k-gap. In both cases, the range where transverse modes operate shrinks to zero. This is an obvious property which Bryk et al have unfortunately missed.

4. Bryk et al choose to employ the FL criterion based on $\tau \approx \tau_{\rm D}$ to discuss the FL and cite our earlier Ref. [3] to back this up. Bryk et al choose not to mention (a) our statement that this criterion was stated as an approximate relationship rather as the exact equality (see Eq. (1) in Ref. [3]) and (b) our discussion (first page of Ref. [4]) that this criterion, although qualitatively convenient to discuss the underlying physics, it not suited for quantitative estimations because there is a degree of flexibility involved in the definition of τ and $\tau_{\rm D}$. We have shown that two quantitative criteria of the FL are based on the velocity autocorrelation function and $c_v = 2$ ($k_{\rm B} = 1$). The two criteria give coinciding FL [4]. An appropriate choice of τ and $\tau_{\rm D}$ results in the corresponding line being close to the FL calculated using the two criteria above.

We note that the criterion $c_v = 2$ applies to harmonic or quasi-harmonic systems, where each mode contributes T (or close to it) to the energy. Bryk et al incorrectly apply this result to the hard-spheres system [12], the system known to be absolutely anharmonic. In the hard-spheres system, particles move outside the range of interaction between collisions, with associated zero potential energy. Consequently, formally calculated collective excitations in the hard-sphere systems are known to be unrelated to harmonic modes. As a result, the calculated energies are $\frac{T}{2}$ per mode, giving the textbook result that the specific heat of the hard-spheres system is $\frac{3}{2}$ as in the ideal gas [24].

5. Bryk et al state that the thermodynamic definition of the FL $c_v = 2$ ($k_{\rm B} = 1$) corresponding to the disappearance of transverse modes is inconsistent with the way of calculating the energy of transverse modes E_t as

$$E_t = \int\limits_{\omega=\frac{1}{\tau}}^{\omega_{\rm D}} E(\omega, T)\frac{6N}{\omega_D^3}\omega^2 d\omega \qquad (1)$$

where $g(\omega) = \frac{6N}{\omega_D^3}\omega^2$ is the density of states of transverse modes. The stated reason is that the lower integral limit in (1) is in k-space rather in frequency.

Bryk et al are aware that we discussed the gap in k-space [22, 23] and previous related developments but choose not to mention our discussion. Indeed, in our recent paper [23] we have cited the theoretical derivation of the gap by Boon and Yip [18] which precedes the gap references in Bryk et al paper.

Notably, Eq. 24 in the cited paper by Bryk (T. Bryk 2011, Ref. [25]) gives the k-gap as $k_g = \left(\frac{\rho G}{\eta}\right)^{\frac{1}{2}}$. This is contradicted by earlier work [18] and our own analysis

[22] giving k_g as $k_g = \frac{1}{2c\tau}$ which can not be reduced to k_g derived by Bryk using the Maxwell relationship and $G = \rho c^2$. In fact, k_g derived by Bryk does not have the correct dimensionality of inverse meter and therefore can not be used in any practical evaluations of the gap.

In stating their argument, Bryk et al choose not to mention our previous result [23] known to them, namely that E_t calculated as (1) gives the result identical to E_t calculated as an integral in $k-$space accounting for the k-gap as

$$E_t = \int_{k_g=\frac{1}{c\tau}}^{k_\mathrm{D}} E(\omega,T)\frac{6N}{k_\mathrm{D}^3}k^2dk \qquad (2)$$

Both (1) and (2) give the identical result in the classical case $E = T$:

$$E_t = 2NT\left(1-\left(\frac{\omega_\mathrm{F}}{\omega_\mathrm{D}}\right)^3\right) \qquad (3)$$

which is easy to understand because the lower limit in (2) $k_g = \frac{1}{c\tau}$ [23] corresponds in the Debye model $\omega = ck$ (the Debye model is as applicable to liquids as it is to solids [26]) to Frenkel frequency $\omega_\mathrm{F} = \frac{1}{\tau}$, the lower limit in (1).

Bryk et al subsequently propose to evaluate E_t as an integral over frequency with zero lower limit. This is not necessary because E_t in (2) involves k-space of phonons and is therefore a primary calculation. However, if one wishes so the integral over frequency can be evaluated as

$$E_t = \int_0^{\sqrt{c^2k_\mathrm{D}^2-\frac{1}{\tau^2}}} E(\omega,T)\frac{6N}{\omega_D^3}\omega\sqrt{\omega^2+\frac{1}{\tau^2}}d\omega \qquad (4)$$

where $g(\omega) \propto \omega\sqrt{\omega^2+\frac{1}{\tau^2}}$ is the density of states corresponding to the k-gap dispersion relationship $\omega = \sqrt{c^2k^2-\frac{1}{\tau^2}}$ [22, 23]. This gives the result identical to (3) as expected, where $\omega_\mathrm{D} = ck_\mathrm{D}$.

The above results were communicated to T. Bryk and G. Ruocco prior to submission of Bryk et al paper [13].

Importantly, notwithstanding the selective showing of results of E_t by Bryk et al, the discussion of how E_t decreases with temperature is unimportant for the thermodynamic criterion of the FL $c_v = 2$. Indeed, the disappearance of two transverse modes implies that c_v, in addition to the kinetic term $\frac{3}{2}$, has the contribution of $\frac{1}{2}$ from the potential term of the remaining longitudinal mode, giving $c_v = 2$. This was discussed by Brillouin in his 1964 book [27].

In this regard, we note that the earlier data of Bryk et al (their Ref. 7) confirm the thermodynamic criterion of the FL $c_v = 2$: the crossover of PSD is seen when c_v is close to 2 ($c_v = 1.92$).

We now make two remarks regarding erroneous points of secondary importance made by Bryk et al:

(a) Contrary to what is stated, the book by Widom (Ref. 5 in Bryk et al) does not discuss the Widom line.

(b) Bryk et al state that the fact that the FL crosses the boiling line below the critical point results in a contradiction. Bryk et al fail to note a well-known fact (see, e.g., [28]) that close to the critical point, the liquid phase does not exist as a condensed matter state. Instead, the state at temperatures around (0.8-1)T_c corresponds to the gas state from the point of view of both dynamics and thermodynamics. On a similar point, Bryk et al state "Obviously, any separation line of liquid-like and gas-like types of dynamics of supercritical fluids must emanate from the critical point." Bryk et al are well aware that this is not obvious: one of the authors in Bryk et al paper was a co-author on the earlier paper [29] where the change of dynamics was observed near (0.7-0.8)T_c.

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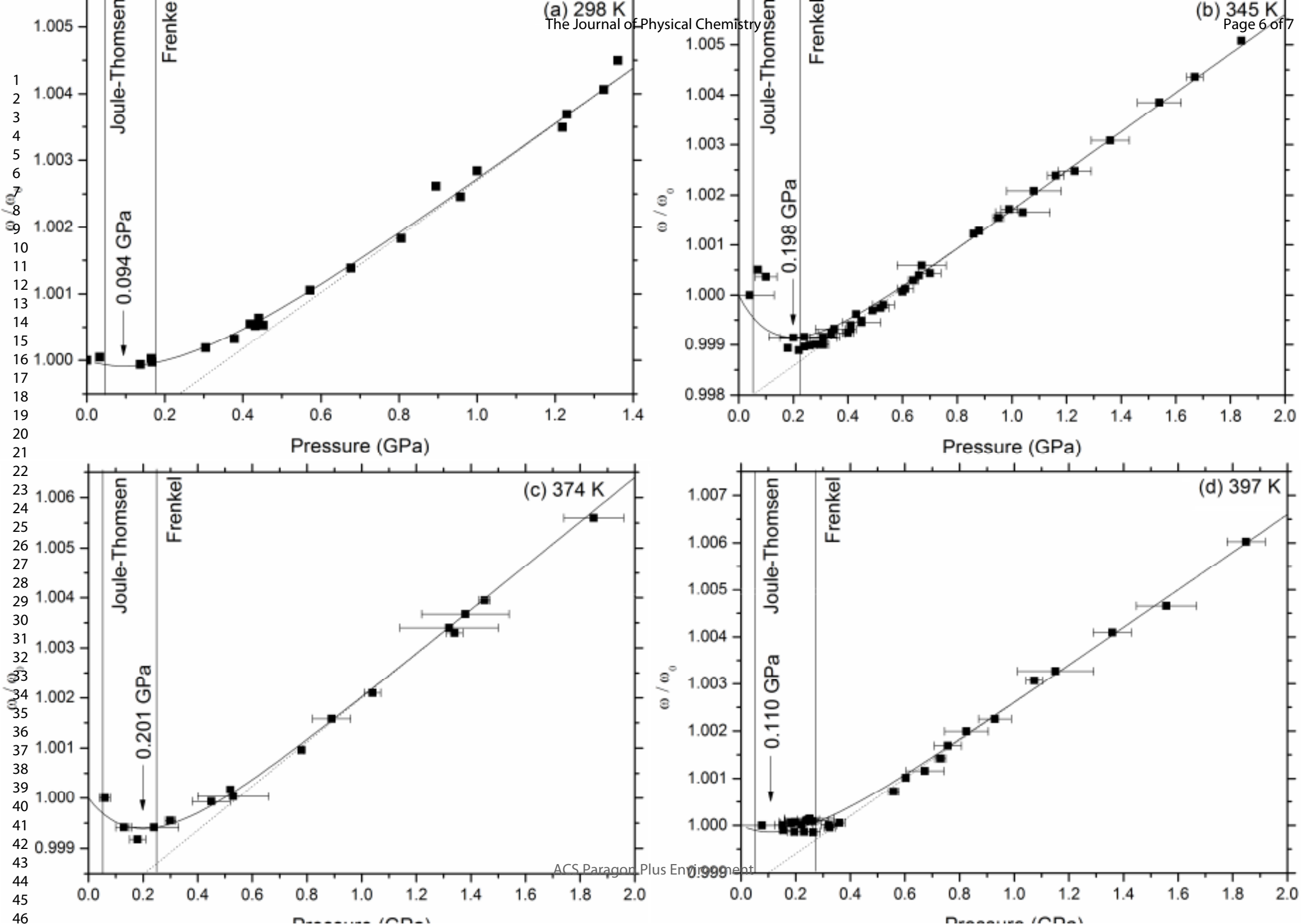
(a) 298 K
Joule-Thomsen
Frenkel
0.094 GPa
ω / ω0
Pressure (GPa)
(b) 345 K
Joule-Thomsen
Frenkel
0.198 GPa
ω / ω0
Pressure (GPa)
(c) 374 K
Joule-Thomsen
Frenkel
0.201 GPa
ω / ω0
Pressure (GPa)
(d) 397 K
Joule-Thomsen
Frenkel
0.110 GPa
ω / ω0
Pressure (GPa)