

Emergence and Evolution of the k Gap in Spectra of Liquid and Supercritical States

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Fundamental understanding of strongly interacting systems necessarily involves collective modes, but their nature and evolution is not generally understood in dynamically disordered and strongly interacting systems such as liquids and supercritical fluids. We report the results of extensive molecular dynamics simulations and provide direct evidence that liquids develop a gap in a solidlike transverse spectrum in the reciprocal space, with no propagating modes between zero and a threshold value. In addition to the liquid state, this result importantly applies to the supercritical state of matter. We show that the emerging gap increases with the inverse of liquid relaxation time and discuss how the gap affects properties of liquid and supercritical states.

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Dynamical and thermodynamic properties of an interacting system are governed by collective excitations, or modes. Collective modes have been studied in depth and are well understood in solids and gases. This is not the case for the liquid state where the combination of strong interactions and dynamical disorder has been thought to preclude the development of a general theory [1] including understanding the nature of collective modes.

Collective modes in solids include one longitudinal and two transverse acoustic modes. In gases, the collective mode is one longitudinal long-wavelength sound wave considered in the hydrodynamic approximation. In liquids, collective modes are well understood in the hydrodynamic approximation $\omega\tau < 1$ [2], where ω is frequency and τ is liquid relaxation time, the average time it takes for a molecule to diffuse the distance equal to interatomic separation [3,4]. Importantly, there is a different regime of wave propagation: $\omega\tau > 1$, where waves propagate in the constant-structure environment, i.e., in the solidlike regime. Experiments have reported both indirect and direct evidence for the existence of solidlike waves in liquids and have ascertained that they are essentially different from the hydrodynamic modes [5–17], including those discussed in generalized hydrodynamics [18,19].

The first proposal regarding solidlike waves in liquids was due to Frenkel [3], who proposed that, at times smaller than τ , particles do not jump, and hence the system behaves like a solid. Therefore, for frequencies larger than

$$\omega_F = \frac{1}{\tau}, \quad (1)$$

the liquid supports two transverse acoustic modes, as does the solid (glass or crystal). The longitudinal acoustic mode is unmodified (except for different dissipation laws in regimes $\omega\tau > 1$ and $\omega\tau < 1$ [3]): density fluctuations exist in any interacting medium, and in liquids they have been shown to propagate with

wavelengths extending to the shortest interatomic separation [5,6,10,15–17].

The proposal that liquids are able to support solidlike transverse modes with frequencies extending to the highest frequency implies that liquids are similar to solids in terms of collective excitations. Therefore, main liquid properties such as energy and heat capacity can be described using the same first-principles approach based on collective modes as in solids, an assertion that was considered unusual in the past when no evidence for propagating solidlike modes in liquids existed. Importantly, high-frequency modes are particularly relevant for liquid thermodynamics because, similarly to solids, they make the largest contribution to system's energy and other properties, whereas the contribution of hydrodynamic modes is negligible [20].

Observed in viscous liquids (see, e.g., Refs. [8,9]), high-frequency transverse modes were later studied in low-viscosity liquids on the basis of positive dispersion [6,10,11,13]. More recently, high-frequency transverse modes were directly measured in the form of distinct dispersion branches and verified in computer modeling [5,13–17]. This has been done at constant temperature and τ .

Although Eq. (1) has been the traditional basis for understanding solidlike transverse modes in liquids [21], the crucial question is whether the frequency gap actually emerges in the liquid transverse spectrum as Eq. (1) and the conventional picture [21] predict and as more recent work [22] seems to suggest? Does this gap change with temperature (pressure) as $1/\tau$? Answering these questions directly is essential for fundamental understanding of collective modes in liquids, and for liquid theory in general.

A recent detailed analysis [20] predicts the following dispersion relationship for liquid transverse modes:

$$\omega = \sqrt{c^2 k^2 - \frac{1}{\tau^2}}, \quad (2)$$

where k is the absolute value of the vector in the reciprocal space (the wave vector), c is the speed of transverse sound, and τ is understood to be the full period of the particles' jump motion equal to twice Frenkel's τ .

Interestingly and differently from Eq. (1), Eq. (2) predicts that liquid transverse acoustic modes will develop a *gap in the reciprocal space* between 0 and k_{gap} :

$$k_{\text{gap}} = \frac{1}{c\tau}. \quad (3)$$

Equations (2) and (3) further predict that the k gap will increase with temperature because τ decreases.

It is interesting to discuss why the gap develops in k space rather than in the frequency domain. Equation (2) follows from our solution of the Navier-Stokes equation extended by Frenkel to include the solidlike elastic response of liquids at times shorter than τ . This gives a wave equation with dissipation, from which Eq. (2) follows [20]. A qualitatively similar result can also be inferred from generalized hydrodynamics, where the hydrodynamic transverse current correlation function is generalized to include large k 's and ω 's [19]. The approach assumes that the shear viscosity function K , the memory function for the transverse current correlation function, exponentially decays with time τ , giving a resonant frequency in the correlation function. If we now identify K at short times with c^2 , the resonant frequency becomes similar to Eq. (2). A gap in k space, albeit different from Eq. (3), is also noted in a different method [23]. Using Eq. (3), we write the condition $k > k_{\text{gap}}$ approximately as $\lambda < d_{\text{el}}$, where $d_{\text{el}} = c\tau$ is the liquid elasticity length, the propagation length of a shear wave in the liquid [24]. The microscopic meaning of d_{el} follows from noting that liquid particles jump with a period of τ and hence disrupt the wave continuity at distances larger than $c\tau$, setting the longest wavelength of propagating waves. Therefore, the condition $k > k_{\text{gap}}$ in Eq. (2) is consistent with the condition that allowed wavelengths should be smaller than the wave propagation length [25].

Importantly, we predict that the k gap also emerges in the supercritical state of matter, the state which has traditionally been viewed as a gray area on the phase diagram with unknown properties intermediate between gases and liquids. We previously proposed that solidlike transverse modes should propagate in supercritical fluids below the Frenkel line (FL) [20,30–32]. We therefore predict that supercritical fluids below the FL should also develop the same gap (3) in the transverse spectrum.

The main aim of this Letter is to obtain direct evidence for the gap discussed above. We perform extensive molecular dynamics simulations in different types of liquids and supercritical fluids, including noble and molecular. We find that a gap develops in solidlike transverse acoustic spectrum in reciprocal space which increases with the inverse of liquid relaxation time. These specific results call for new high-temperature and pressure experiments.

We have aimed to study the propagation of solidlike transverse waves in liquids with different structure and

bonding types and have performed molecular dynamics simulations of noble liquid Ar and molecular CO₂ [26]. The pressure was fixed at 40 bar for subcritical Ar, 10 kbar for supercritical Ar, and 9 kbar for supercritical CO₂. The temperature was extended well above critical for the last two systems.

We calculate the propagating transverse modes from transverse current correlation functions [18]: $C(\mathbf{k}, t) = (k^2/N)\langle J_x(-\mathbf{k}, t)J_x(\mathbf{k}, 0) \rangle = (k^2/N)\langle J_y(-\mathbf{k}, t)J_y(\mathbf{k}, 0) \rangle$, where N is the number of particles, transverse currents $J(\mathbf{k}, t) = \sum_{j=1}^N \mathbf{k} \times \mathbf{v}_j(t) \exp[-i\mathbf{k} \cdot \mathbf{r}_j(t)]$, \mathbf{v} is the particle velocity, and the wave vector \mathbf{k} is along the z axis. The spectra of transverse currents are calculated as the Fourier transform of the real part of $C(\mathbf{k}, t)$ [the imaginary part of $C(\mathbf{k}, t)$ is calculated to be zero within the error, as expected]. A smoothing function is often used for the analysis of $C(k, t)$ in order to reduce the noise [16,17]. To get better quantitative and model-free results, we choose not to use the smoothing. Instead, we repeat our simulations 20 times using different starting velocities and average the results. This produces $C(k, t)$ with reduced noise which does not change when the number of simulations is increased. We show examples of $C(k, \omega)$ for different peak frequencies in the Supplemental Material [26].

Our main observation is related to the evolution of dispersion curves. We plot intensity maps $C(k, \omega)$ in Fig. 1 and observe that a *gap* develops in k space and that the range of transverse modes progressively shrinks. A maximum of $C(k, \omega)$ at frequency ω is related to a propagating mode at that frequency and gives a point (k, ω) on the dispersion curve [18]. We plot dispersion curves in Fig. 2 and observe a detailed evolution of the gap. At the highest temperature simulated, $C(k, \omega)$ becomes not easily discernable from the noise.

We observe that the gap k_{gap} develops in all systems simulated. Importantly, the simulated systems where we detect transverse modes extend into the supercritical state: our maximal temperature and pressure correspond to $(205.6P_c, 6.3T_c)$ for Ar and $(122.0P_c, 2.0T_c)$ for CO₂. It has remained unclear whether the supercritical state is able to support solidlike transverse modes at all, but we recently proposed that the supercritical state supports transverse modes below the FL, the line that demarcates liquidlike and gaslike properties on the phase diagram [20,30–32]. Below the Frenkel line, particle motion consists of both oscillatory and diffusive components. Above the line, the oscillatory component of particle motion is lost, leaving only diffusive motion, as in a gas. Approaching the line from below approximately corresponds to τ becoming equal to the shortest period of transverse modes, at which point the system becomes depleted of all available transverse modes, according to Eq. (1). Using the previously calculated FL for Ar [30] and CO₂ [33], we find that the propagating solidlike transverse

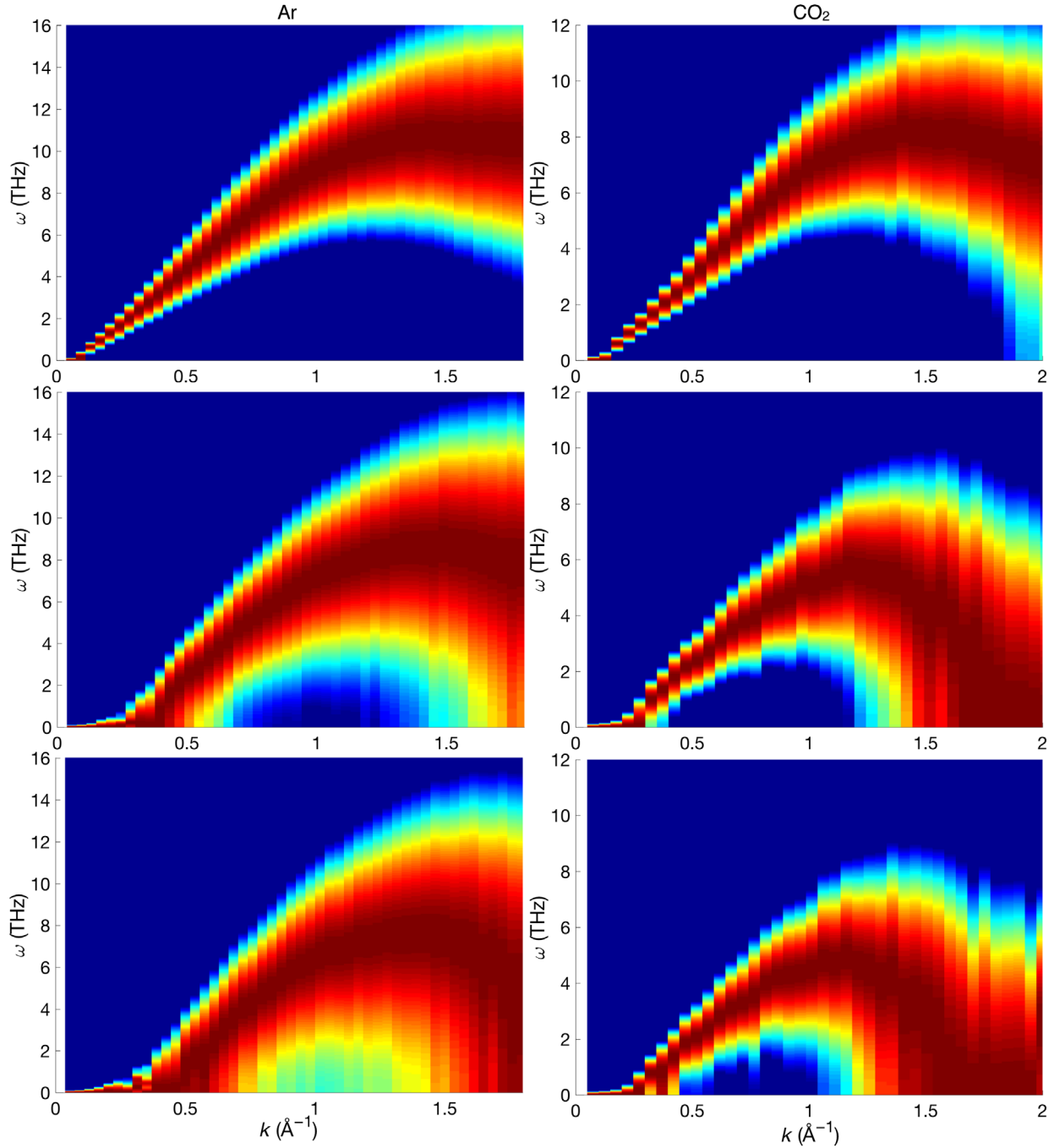


FIG. 1. Intensity maps of $C(k, \omega)$ for supercritical Ar at (top panel) 250 K, (middle panel) 350 K, and (bottom panel) 450 K and supercritical CO_2 at (top panel) 300 K, (middle panel) 400 K, and (bottom panel) 500 K. The maximal intensity corresponds to the middle points of the dark red areas and reduces away from them.

modes reported in Fig. 2 correspond to supercritical Ar and CO_2 below the FL.

We note that the intensity of $C(k, \omega)$ peaks decreases with temperature for all mode frequencies, but lower-frequency peaks decay much faster than higher-frequency ones. In examples shown in the first figure in the Supplemental Material [26], both 2 THz and 8 THz transverse modes show a clear peak at 200 K, but, whereas the peak of the 2 THz mode almost disappears

at 350 K, the 8 THz mode peak remains pronounced. This is consistent with the experiments showing that low-frequency transverse phonons are not detected [5,15].

We also note that reduced peak intensity of $C(k, \omega)$ at very high temperature, together with the persisting noise, can obfuscate the criterion of a propagating mode because a difference between a peak in $C(k, \omega)$ at low temperature and a broad shoulder at high temperature becomes less

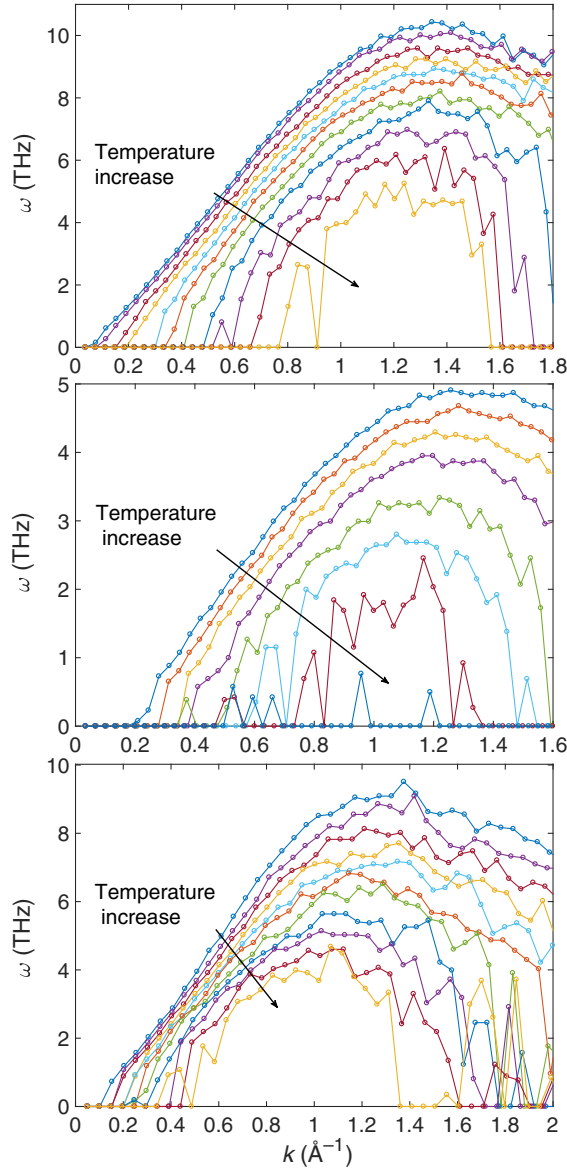


FIG. 2. Phonon dispersion curves of (top panel) supercritical Ar at 200–500 K and 550 K, (middle panel) subcritical liquid Ar at 85–120 K, and (bottom panel) supercritical CO₂ at 300–600 K. The temperature increment is 30, 5, and 30 K for supercritical Ar, subcritical liquid Ar, and supercritical CO₂, respectively. The deviation from linearity (the curving over) of dispersion curves at large k is related to probing the effects comparable to interatomic separations (in the solid, this corresponds to the curving over of $\omega \propto \sin ck$ at large k). This effect is not accounted for in the theory leading to the gap in Eqs. (2) and (3) because the theory is formulated in the continuous medium [20] and therefore describes the k gap in the linear part of the dispersion law. We show k in the range slightly extending the first pseudo zone boundary (FPZB) at low temperature. As volume and interatomic separation increase with temperature, FPZB shrinks, resulting in a decrease of $\omega \propto \sin ck$ at large k beyond the FPZB. This effect is unrelated to the k gap.

pronounced. However, one can also consider the oscillatory behavior of $C(k, t)$ an indicator of a propagating mode. Shown in the second figure in the Supplemental Material [26], $C(k, t)$ for a k close to the Brillouin pseudoboundary

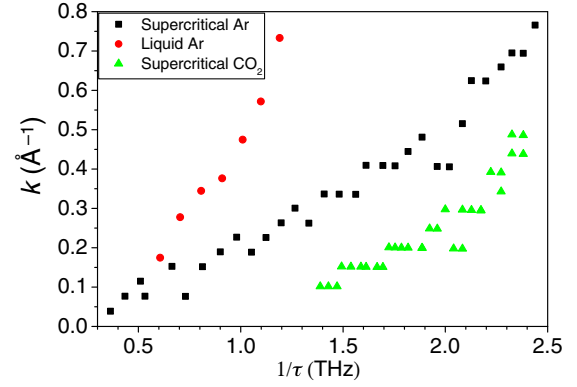


FIG. 3. The width of the k gap vs $1/\tau$ for subcritical liquid Ar in the range 85–115 K, supercritical Ar in the range 200–500 K, and supercritical CO₂ in the range 300–600 K.

has minima and oscillatory behavior at 900 and 950 K but not at 1000 K, even though $C(k, \omega)$ shows no maxima in the temperature range 900–1000 K. In agreement with this, the temperature of the Frenkel line demarcating propagating and nonpropagating transverse modes is about 1000 K [30].

We can now directly verify the predictions for the gap $k_{\text{gap}} = 1/(c\tau)$ in Eq. (3). First, in Fig. 3 we observe either a nearly linear relationship or a correct trend between k_{gap} and $1/\tau$ (more computationally consuming CO₂ with a smaller cell size involves a smaller resolution of k and a larger noise). The increase of the slope of k_{gap} vs $1/\tau$ at large $1/\tau$ at high temperature is expected because c decreases with temperature ($1/c$ increases). Second, we calculate c for each system from the dispersion curves in the linear regime at small k in Fig. 2 and find them to be in reasonable agreement with the c extracted from the linear regime in Fig. 3 for the three systems studied.

Our results are important for understanding liquid thermodynamics. The k gap implies that the energy of transverse modes can be calculated as $E_t = \int_{k_{\text{gap}}}^{k_D} E(k) (6N/k_D^3) k^2 dk$, where N is the number of particles, k_D is the Debye wave number, and the factor $6N/k_D^3$ is due to $2N$ transverse modes between 0 and k_D in the solid. Taking $E(k) = k_B T$ in the classical case gives

$$E_t = 2Nk_B T \left[1 - \left(\frac{\omega_F}{\omega_D} \right)^3 \right], \quad (4)$$

where $\omega_D = ck_D$ is the Debye frequency.

The same result can be obtained in the Debye model if we calculate the energy of transverse modes propagating above the frequency ω_F as Eq. (1) predicts, i.e., if we consider a gap in the frequency spectrum. Indeed, this energy can be written as $\int_{\omega_F}^{\omega_D} g(\omega) k_B T d\omega$, where $g(\omega) = (6N/\omega_D^3)\omega^2$ is the Debye density of states of the transverse modes. This gives the same E_t as in Eq. (4). As ω_F increases with temperature, the number of transverse modes decreases, resulting in the decrease of specific heat, in agreement with the experimental results for many liquids

and supercritical fluids in a wide temperature range [20,34]. Hence, from the point of view of thermodynamics, the transverse modes can be considered to have a frequency gap ω_F , in agreement with the original assumption (1).

Writing (2) as

$$E = \sqrt{p^2 c^2 - E_F^2} \quad (5)$$

where $E = \hbar\omega$ and $E_F = \hbar\omega_F$, we see that quasiparticles with energy E_F act as filters to suppress the quasiparticle excitations whose energy pc is below E_F . We propose that the energy-momentum relationship (5) may be of interest in other areas of physics including quantum field theory.

In summary, we showed that collective modes in liquids and supercritical fluids develop a k gap in the solidlike transverse spectrum.

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