

Vibrational Phase Relaxation along the Critical Isochore of Nitrogen: The Role of Local Density Fluctuations in the Rate Enhancement

Swapan Roychowdhury and Biman Bagchi*

Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore-560012, India

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Vibrational dephasing of the nitrogen molecule is known to show highly interesting anomalies near its gas-liquid critical point. Here we present theoretical and computational studies of the Raman linewidth of nitrogen along the critical isochore. The linewidth is found to have a lambda-shaped temperature dependence near the critical point. As observed in experimental studies, the calculated line shape becomes Gaussian as the critical temperature (T_c) is approached. Both the present simulation and a mode coupling theory analysis show that the slow decay of the enhanced density fluctuations near the critical point, probed at the subpicosecond time scales by vibrational frequency modulation, along with an enhanced vibration-rotation coupling, are the main causes of the observed anomalies.

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As the gas-liquid critical point of a fluid is approached, several dynamical properties of the system, such as the thermal conductivity, the bulk viscosity, the linewidth of the central Rayleigh spectrum, show anomalous behavior. This behavior is collectively known as *critical slowing down* [1] and is physically explained by exploiting the divergence of the correlation length and using the dynamic mode coupling theory (MCT) [2,3]. In the recent years, several anomalies have also been observed in molecular relaxation processes near the critical point or in the supercritical fluid. One of them is the surprising augmentation of the solvent density around a solute [4]. Another interesting case is the vibrational phase relaxation which shows more than one anomaly, yet to be understood.

Clouter *et al.* [5] found that the isotropic Raman line shape of a simple fluid like N_2 exhibits a remarkable additional nonrotational broadening (i.e., *increase* in dephasing rate) near the gas-liquid critical points (ρ_c, T_c). They measured the Raman spectra along the triple point to the critical point and the behavior of the line shape as the critical point is approached from above. Recently Musso *et al.* [6] measured the temperature dependence of the line shape parameters (i.e., shift, width, and asymmetry) along both the coexistence line and the critical isochore of liquid nitrogen and found that the temperature dependent linewidth (Γ) is lambda-shaped. The line shape was found to undergo a change from Lorentzian (away from T_c) to Gaussian (near T_c).

The observation of such anomalies has, till now, defied a convincing explanation. Mukamel, Stern, and Ronis [7] had earlier interpreted the rapid broadening of Raman line shape as a manifestation of dynamical critical phenomena. This interpretation raises the following questions. As the microscopic time correlation function involved decays in less than a picosecond (actually in about 200 fs), why and how are the slow long wavelength density fluctuations important and relevant? The physics

here is clearly different from the one involved in the critical slowing down at the long wavelengths.

In a recent investigation, vibrational phase relaxation of the fundamental and lower overtones of the N-N stretch in pure nitrogen was simulated by molecular dynamics (MD) simulations, and the MCT [8] was used to explain the simulation results. This study could reproduce the rapid rise in dephasing rate as the critical point is approached along the coexistence line, although it did not include the vibrational coordinate (q) dependence of the interatomic potential and ignored the cross term between the vibration-rotation coupling and force and their derivatives. Everitt and Skinner [9] studied the Raman line shape of nitrogen in a systematic way by including the bond length dependence of the dispersion and repulsive force parameters along the coexistence line of nitrogen. They also incorporated the cross-correlation terms which were neglected earlier. Their results for the line shifts and linewidths along the gas-liquid coexistence of N_2 are in good agreement with experimental results. These theoretical studies did *not* consider dephasing along the *critical isochore*. In addition, a convincing picture of anomalies did not emerge. The results presented in this Letter provide the first microscopic explanation of the above anomalies.

The theories of the vibrational dephasing are all based on Kubo's stochastic theory of the line shape [10], extended to the study of vibrational dephasing by Oxtoby [11]. The isotropic Raman line shape, $I(\omega)$, is the Fourier transform of the normal coordinate time correlation function, $C_Q(t)$ [11],

$$I(\omega) = \int_0^\infty \exp(i\omega t) [\langle Q(t)Q(0) \rangle]. \quad (1)$$

A cumulant expansion of Eq. (1) followed by truncation after second order gives the following well-known expression of $C_Q(t)$ [12]:

$$\begin{aligned} \langle Q(t)Q(0) \rangle &= \text{Re} \exp(i\omega_0 t + i\langle \Delta\omega \rangle t) \\ &\times \exp \left[- \int_0^t dt' (t-t') \langle \Delta\omega(t') \Delta\omega(0) \rangle \right]. \end{aligned} \quad (2)$$

The frequency modulation time correlation function, $C_\omega(t) = \langle \Delta\omega(t) \Delta\omega(0) \rangle$, derives contributions from the atom-atom, the resonance, the vibration-rotation (VR) coupling, and also the cross terms [11]. We calculated the linewidth, the line shape, and the dephasing time of N_2 for different thermodynamical state points of nitrogen, along both the coexistence line and the critical isochore, using Eqs. (1) and (2).

The Hamiltonian of homonuclear diatomic molecules can be written as $H(\vec{q}) = H_v + T(\vec{q}) + U(\vec{q})$, where H_v is the vibrational Hamiltonian, $T(\vec{q})$ is the total translational and rotational kinetic energy, $U(\vec{q})$ is the intermolecular potential energy, and \vec{q} is the collection of vibration coordinates q_i . The intermolecular potential energy is the sum of the following site-site (v_{ij}) between two molecules i and j [9]. The total intermolecular potential energy is taken to be

$$\begin{aligned} U(\vec{q}) &= \frac{1}{2} \sum_{i \neq j} \sum_{\alpha\beta} v_{ij}(\epsilon_{i\alpha}, \sigma_{i\alpha}, r_{i\alpha j\beta}) \\ &= \frac{1}{2} \sum_{i \neq j} \sum_{\alpha,\beta}^{1,2} 4\epsilon_{i\alpha j\beta} \left[\left(\frac{\sigma_{i\alpha j\beta}}{r_{i\alpha j\beta}} \right)^{12} - \left(\frac{\sigma_{i\alpha j\beta}}{r_{i\alpha j\beta}} \right)^6 \right], \end{aligned} \quad (3)$$

where $r_{i\alpha j\beta} = |\vec{r}_{j\beta}(q_j) - \vec{r}_{i\alpha}(q_i)|$ and $\vec{r}_{j\beta}(q_j) = \vec{r}_{j\beta}(0) + \hat{r}_{j\beta} q_j / 2$. $\vec{r}_{j\beta}(q_j)$ is the position of the nucleus of atom β in molecule j , and $\hat{r}_{j\beta}$ is the unit vector oriented from the center of mass of molecule j to the β th atom. The vibrational coordinate dependence of Lennard-Jones (L-J) parameters are given by $\epsilon_{i\alpha j\beta} = \sqrt{\epsilon_{i\alpha} \epsilon_{j\beta}} = \epsilon(1 + \gamma q_i + \gamma q_j + 2\gamma^2 q_i q_j)$ and $\sigma_{i\alpha j\beta} = \left(\frac{\sigma_{\alpha\alpha} + \sigma_{\beta\beta}}{2} \right) = \sigma(1 + \delta q_i + \delta q_j)$. We use the linear expansion coefficients γ and δ as determined by Everitt and Skinner [9,13].

Microcanonical MD simulations [14] were carried along the coexistence line and along the critical isochore using the leapfrog algorithm for different thermodynamical state points of nitrogen. A system of 256 diatomic particles was enclosed in a cubic box, and periodic boundary conditions were used. In simulation, the system was allowed to equilibrate for 100 000 time steps with $\Delta t = 0.0002\tau$, where $\tau = \sqrt{(m\sigma^2/\epsilon)}$, m being the mass of the molecule] is found to be equal to 3.147 ps. The averages were calculated over 400 000 MD steps. The thermodynamic state of the system can be expressed in terms of the reduced density of $\rho^* = \rho\sigma^3$ and a reduced temperature of $T^* = k_B T/\epsilon$. The density of the system has been expressed in terms of the number of molecules per unit volume times σ^3 , and the temperature is in units of ϵ/k_B , where σ and k_B are the Lennard-Jones diameter of the molecule and the Boltzmann constant, respectively.

A limited number of simulations have been done with $N = 512$ molecules. We found no significant difference in the linewidth at the larger system.

Figure 1 shows both the simulated temperature dependent dephasing rate of nitrogen and also the experimental one. The solid squares are the linewidth for different state points along the coexistence curve of nitrogen, and the solid circles are the linewidth along the critical isochore. The interesting feature in the figure is the lambda-shaped linewidth when the values for two different regions of nitrogen are presented together. This figure is similar to the one observed experimentally (see Fig. 4 of Ref. [6]). It is interesting to note the sharp rise in the dephasing rate as the CP is approached. There are noticeable differences in the high temperature region along the critical isochore.

To understand the origin of this critical behavior, we carefully analyzed each of the six terms [15] (three autocorrelations and three cross terms between density, vibration-rotation coupling, and resonance), which are responsible for the modulation of the vibrational frequency for fundamental transition. Two terms are found to dominate near the CP , and these are the density and the vibration-rotation coupling. The temperature dependence of these two terms are shown in Fig. 2 where the integrand of Eq. (2), $X_{ij}(t) = \int_0^t dt'(t-t')C_\omega^{ij}(t')$, is plotted against time for seven state points along the critical isochore, where i, j represent the density, VR coupling, and resonance terms, respectively. Note the sharp rise in the value of the integrand as the critical temperature is approached, and the fall when it is crossed. We have found that both these contributions at the CP are distinct

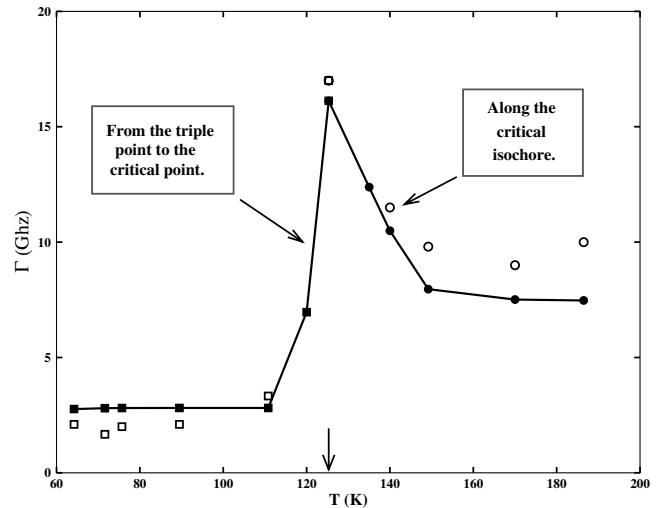


FIG. 1. The simulated lambda-shaped linewidth (Γ) of nitrogen along the coexistence line (solid squares) and the critical isochore (solid circles). The experimental results for the linewidth along the coexistence line (open squares) and the critical isochore (open circles) reported by Clouter and Kieft and by Chesnoy in Ref. [5] are also shown. The CP is indicated by an arrow on the abscissa.

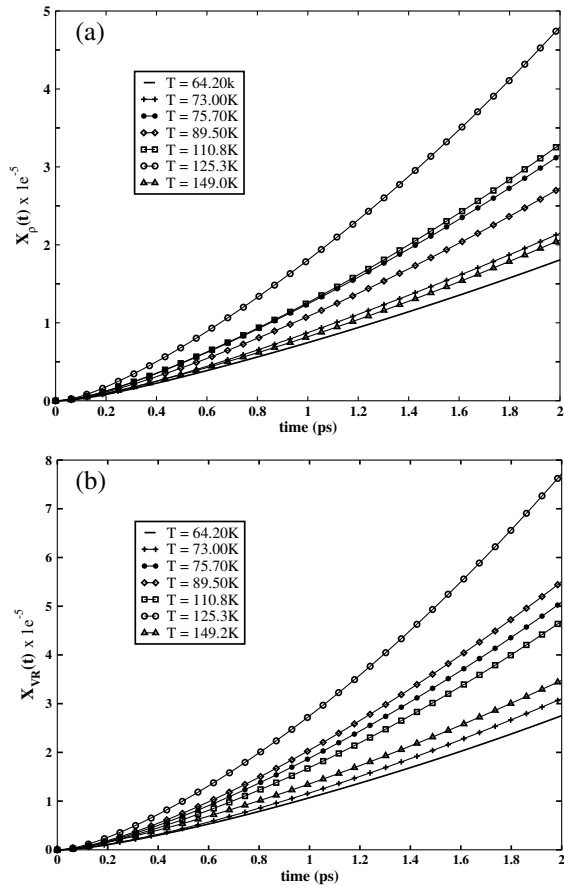


FIG. 2. The time dependence of the relative contributions of the (a) density-density, $X_\rho(t)$, and (b) VR coupling, $X_{VR}(t)$, terms at different temperatures along the critical isochore.

compared to the other state points. Thus, the rise and fall of the dephasing rate arises partly from the rise and fall in the density and the vibration-rotation terms.

A crossover from the Lorentzian-like to Gaussian line shape can happen when the usually large separation in the time scales of decay of $C_\omega(t)$ and $C_Q(t)$ [6,11] ceases to exist and the two time correlation functions begin to overlap. Indeed, the computed line shape becomes Gaussian near that from CP . Note that the frequency modulation time correlation function decays fully in about 200 fs.

What could be the reason for this dramatic crossover behavior? The increase in density fluctuations [7,16] near the CP increases the magnitude of the mean square frequency fluctuation $\langle \Delta\omega_\rho^2 \rangle$. This leads itself to an increase in the rate of decay of the normal coordinate time correlation function, $[C_Q(t)]$. In addition, the frequency modulation time correlation function slows down somewhat. As the decay of these two time correlation functions becomes comparable, the line shape goes over to the Gaussian form. This is a novel effect and is different from that commonly encountered.

If one considers only the number density as the relevant slow variable in dephasing, then MCT analysis gives the

following expression for the density dependence frequency modulation time correlation function [17]:

$$\langle \Delta\omega_\rho(0)\Delta\omega_\rho(t) \rangle = \frac{(k_B T)^2}{6\pi^2 \hbar^2 \rho} \int_0^\infty k^2 dk F_s(k, t) C^2(k) F(k, t), \quad (4)$$

where $C(k)$ is the Fourier transform of two particle direct correlation function. Near CP , the main contribution is derived from the long wavelength (that is, small k) region, where the self-intermediate scattering function is $F_s(k, t) = e^{-D_s k^2 t}$, the intermediate scattering function is $F(k, t) = S(k) e^{-D_T k^2 t}$, D_s is the self-diffusion coefficient, $S(k)$ is the static structure factor, and D_T is the thermal diffusivity. Thus, $\langle \Delta\omega_\rho(0)\Delta\omega_\rho(t) \rangle \approx S(k \rightarrow 0) e^{-(D_s + D_T) k^2 t}$. Near CP , $S(k \rightarrow 0)$ becomes very large (as compressibility diverges at $T = T_c$), leading towards a Gaussian behavior for line shape. D_T also undergoes a slowdown near T_c . This complex dependence may lead to a Levy distribution from time dependence of $\langle Q(0)Q(t) \rangle$ as discussed earlier by Mukamel *et al.* [7]. However, a limitation of the above analysis is the absence of the VR term which contributes significantly and may mask some of the critical effects. At high temperature, the latter dominates over the density term. A complete Lorentzian behavior is predicted only in the low temperature liquid phase. Interestingly, the predicted divergence of $\langle \Delta\omega^2(0) \rangle$ very close to T_c enhances the rate of dephasing, and this shifts the decay of $\langle Q(t)Q(0) \rangle$ to short times, giving rise to the Gaussian behavior. We shall return to this point later. We have used MCT to demonstrate that the large enhancement of vibration-rotation coupling near the gas-liquid critical point arises from the non-Gaussian behavior of density fluctuation, and this enters through a nonzero value of the triplet direct correlation function.

To further explore the origin of these anomalous critical temperature effects, we have investigated for the presence of dynamical heterogeneities in the fluid at three temperatures near the CP , by calculating the well-known non-Gaussian parameter $\alpha(t)$ defined as [18] $\alpha(t) = \frac{\langle \Delta r^4(t) \rangle}{3 \langle \Delta r^2(t) \rangle^2} - 1$, where $\langle \Delta r^2(t) \rangle$ is the mean squared displacement and $\langle \Delta r^4(t) \rangle$ the mean quartic displacement of the center of mass of nitrogen molecule. It can approach zero (and hence Gaussian behavior) only for times exceeding the time scale required for individual particles to sample their complete kinetic environments. As can be seen from Fig. 3, the function $\alpha(t)$ is large near CP at times 0.5–5 ps, indicating the presence of long lived heterogeneities near T_c .

The contribution of the density term reflects the combined effects of collisions, repulsive and attractive interactions on the friction on the bond. This term naturally grows as the CP is approached. The rise in the contribution of the vibration-rotation term has a different origin. This increase is due to the slowing down of the rotational time correlation function near the CP [19]. As

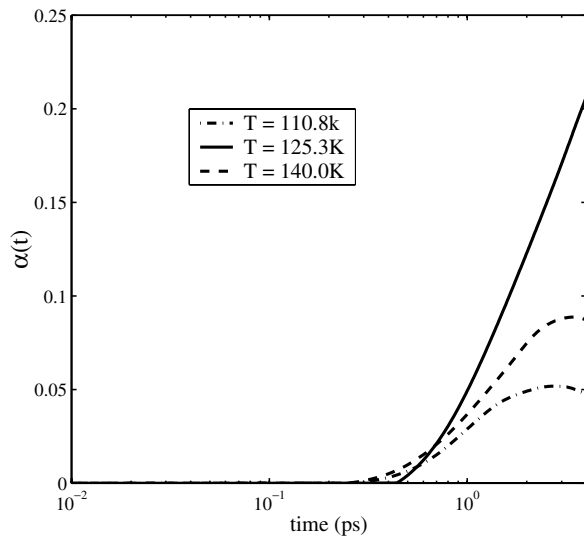


FIG. 3. The non-Gaussian parameter $\alpha(t)$ is plotted against time (t) at three different temperatures along the critical isochore.

we approach the *CP*, the number of molecules having slow decay of rotational time correlation function increases. While one can describe the average effect of density fluctuation through the divergence of the static structure factor $S(k)$ at small wave numbers (as discussed above), this approach does not capture the full scenario. This is because the decay of the frequency modulation time correlation function [$C_\omega(t)$] occurs in the femto-second time scale. At that time scale, the density fluctuation is nearly static. Thus, vibrational dephasing provides snapshots of the large density fluctuations present near the critical temperature. Even more interesting is the origin of the ultrafast decay of $C_\omega(t)$ —this is partly due to the cancellation which arises from the cross terms of VR coupling with the density and the resonance terms. These terms have sign opposite to the pure terms but have comparable magnitude, leading to further enhancement in the rate of decay of $C_\omega(t)$. The reason for such large negative cross correlation can be understood in terms of the inhomogeneity. Note that critical anomaly is nearly absent in CF_4 , CH_4 , and CO_2 . While cubic symmetry in the the former two precludes VR coupling, CO_2 may be too heavy for VR to be important.

It is indeed surprising that our simulations could capture many of the novel features observed in experiments, including the lambda-shaped temperature dependence of the dephasing rate and the crossover from the Lorentzian to the Gaussian form. Large density fluctuations near T_c shifts the dynamics probed to subpicosecond times. This, combined with VR coupling, gives rise to the observed anomalies.

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*Corresponding author.

Email address: bbagchi@sscu.iisc.ernet.in

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