Vibrational dephasing of 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 lineshape becomes Gaussian as the critical temperature ($T_c$) is approached. Both the present simulation and a mode coupling theory (MCT) analysis show that the slow decay of the enhanced density fluctuations near the critical point (CP), probed at the sub-picosecond time scales by vibrational frequency modulation, along with an enhanced vibration-rotation coupling, are the main causes of the observed anomalies.

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 behaviour. This behaviour is collectively known as critical slowing down and is physically explained by exploiting the divergence of the correlation length and using the dynamic mode coupling theory (MCT)\cite{3, 4}. 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\cite{5}. Another interesting case is the vibrational phase relaxation which shows more than one anomaly, yet to be understood.

In their experiments, Clouter et al.\cite{6} found that the isotropic Raman lineshape of a simple fluid like $N_2$ exhibits a remarkable additional non-rotational broadening near the gas-liquid critical points ($\rho_{crit}$, $T_{crit}$). They measured the Raman spectra along the triple point to the critical point and the behaviour of the lineshape as the critical point is approached from above. Recently Musso et al.\cite{7} measured the temperature dependence of the lineshape parameters (i.e shift, width and asymmetry) both along the coexistence and the critical isochore of liquid nitrogen and found that the temperature dependent linewidth ($\Gamma$) is $\lambda$ shaped. The lineshape was found to undergo a change from Lorentzian (away form $T_c$) to Gaussian (near $T_c$).

The observation of such anomalies has, till now, defied a convincing explanation. Mukamel, Stern and Roni\cite{8} had earlier interpreted the rapid broadening of Raman lineshape 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 the overtones of the N-N stretch in pure nitrogen was simulated by MD simulations, and the mode coupling theory (MCT)\cite{9} 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 co-existence line, although it didn’t include the vibrational coordinate($q$) dependence of the inter-atomic potential and ignored the cross-term between the vibration-rotation coupling and force and their derivatives. Everitt and Skinner\cite{10} studied the Raman lineshape of nitrogen in a systematic way by including of 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 lineshifts 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 first microscopic explanation of the above anomalies.

The theories of the vibrational dephasing are all based on Kubo’s stochastic theory of the lineshape\cite{11}, extended to the study of vibrational dephasing by Oxtoby\cite{12}. The isotropic Raman lineshape, $I(\omega)$, is the Fourier transform of the normal coordinate time correlation function, $C_Q(t)$\cite{12},

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

\textbf{Molecular Dynamics Simulation of Vibrational Phase Relaxation along the Critical Isochore of Nitrogen : The Role of Local Density Fluctuations}

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

\[
< Q(t)Q(0) > = Re \exp(i\omega_0t + i < \Delta \omega > t)
\times \exp \left[ - \int_0^t dt' \langle t - t' \rangle < \Delta \omega (t') \Delta \omega (0) > \right]. \tag{2}
\]

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

The Hamiltonian of homonuclear diatomic molecules can be written as

\[
H(\vec{q}) = H_v + T(\vec{q}) + U(\vec{q}), \tag{3}
\]

where \( H_v \) is the vibrational Hamiltonian, \( T(\vec{q}) \) is the total translational and rotational kinetic energy, \( U(\vec{q}) \) is the inter-molecular potential energy, and \( \vec{q} \) is the collection of vibration coordinates \( q_i \). The inter-molecular potential energy is sum of the following site-site \( (\vec{r}_{ij}) \) between two molecules \( i \) and \( j \). The total intermolecular potential energy is taken to be

\[
U(\vec{q}) = \frac{1}{2} \sum_{i \neq j} \sum_{\alpha \beta} n_{ij} \left( \epsilon_{ij}, \sigma_{ij}, r_{i\alpha j\beta} \right) = \frac{1}{2} \sum_{i \neq j} \sum_{\alpha \beta} ^{1, 2} 4 \epsilon_{i\alpha j\beta} \left[ \frac{\sigma_{i\alpha j\beta}}{r_{i\alpha j\beta}} \right] ^{12} - \left[ \frac{\sigma_{i\alpha j\beta}}{r_{i\alpha j\beta}} \right] ^6 \tag{4}
\]

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

Microcanonical (NVE) MD simulations were carried along the coexistence line and along the critical isochore using the leap-frog 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 \( \Delta t = 0.00002 \tau \), where \( \tau = \sqrt{(ma^2/\epsilon)} \), \( m \) being the mass of the molecule. \( \tau \) 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 \( \rho^* = \rho a^3 \) and a reduced temperature of \( T^* = k_B T/\epsilon \). The density of the system has been expressed in terms of number of molecules per unit volume times \( \sigma^3 \) and the temperature is in units of \( \epsilon/k_B \). Where \( \sigma \) and \( k_B \) is the Lennard-Jones diameter of the molecule and is the Boltzmann constant, respectively. 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 figure 4 of Ref. 7). It is interesting to note the sharp rise in the dephasing rate as the CP is approached. There are noticeable difference in the high temperature region along the critical isochore.

To understand the origin of this critical behaviour, we carefully analyzed each of the six terms (three auto correlations 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 figure 2 where the integrand of Eq. 2, \( X_{ij}(t) = \int_0^t dt' \langle t - t' \rangle C_{ij}(t') \), is plotted against time for seven state points along the critical isochore. Where \( i, j \) represents the density(den), vibration-rotation coupling(VR) and resonance(Rs) 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 compared to the other.
state points. Thus, the rise and fall of dephasing rate arises partly from the rise and fall in the density and the vibration-rotation terms.

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

What could be the reason for this dramatic crossover behaviour? The increase in density fluctuations near the CP increases the magnitude of the mean square frequency fluctuation \( \langle \Delta \omega^2 \rangle \). 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 become comparable, the lineshape goes over to the Gaussian form. This a novel effect and different from that commonly encountered.

If one considers only the number density as the relevant slow variable in dephasing, then mode coupling theory analysis (MCT) gives the following expression for the density dependence frequency modulation time correlation function \[5\]:

\[
\langle \Delta \omega_\mu(0) \Delta \omega_\mu(t) \rangle = \frac{k_B T}{6\pi^2 \hbar^2 \rho} \int_0^\infty k^2 dk C(k)^2 F(k,t).
\]

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 self-intermediate scattering function, \( F_s(k,t) = e^{-D_s k^2 t} \) and intermediate scattering function, \( F(k,t) = S(k)e^{-D_T k^2 t} \). \( D_s \) is the self-diffusion coefficient, where \( S(k) \) is the static structure factor, and \( D_T \) is the thermal diffusivity. Thus, \( \langle \Delta \omega_\mu(0) \Delta \omega_\mu(t) \rangle \approx S(k \to 0)e^{-D_s k^2 t} \). Near CP, \( S(k \to 0) \) becomes very large (as compressibility diverges at \( T = T_c \)), leading towards a Gaussian behaviour for lineshape. \( D_T \) 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.\[8\]. 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 behaviour 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 behaviour.

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 non-zero 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 \[10\]:

\[
\alpha(t) = \frac{\langle r^4(t) \rangle}{3 \langle r^2(t) \rangle^2} - 1 \text{ where } \langle \Delta r(t)^2 \rangle \text{ is the mean squared displacement and } \langle \Delta r(t)^4 \rangle \text{ the mean quartic displacement of the center of mass of nitrogen molecule. It can only approach zero (and hence Gaussian behaviour) for times exceeding the time scale required for individual particles to sample their complete kinetic environments. As can be seen from figure 3, the function } \alpha(t) \text{ is large near CP at times } 0.5 - 5 \text{ ps, indicating the presence of long lived heterogeneities near } T_c.
\]

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\[20\]. As 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 wavenumbers (as discussed above), this approach does not capture the full scenario. This is because the decay of the frequency modulation time correl-
ultrafast decay of $C_v(t)$—this is partly due to the cancelation 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 $C_v(t)$. 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 $CO_2$[21]. 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 cross-over from the Lorentzian to the Gaussian form. Large density fluctuations near $T_c$ shifts the dynamics probed to sub-picosecond times. This combined with VR coupling, give rise to the observed anomalies.

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