

# Criterion for the observation of the critical contribution to vibrational bands in fluids

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Light scattering has long been a probe for density fluctuations and their dynamics near gas-liquid critical points and for concentration fluctuations and their dynamics near binary-mixture critical points. More recently, several groups have measured the widths of Raman-active vibrational transitions near these critical points. To extract critical point information from the widths, the measurements were analyzed in the form  $\Delta\nu = c\epsilon^{-x} + \Delta\nu_0$ , where  $\Delta\nu$  is the band or linewidth,  $\epsilon = |(T - T_c)/T_c|$ ,  $x$  an unknown exponent,  $c$  a constant, and  $\Delta\nu_0$  a noncritical contribution to the linewidth. The results were found to vary substantially from system to system. In some cases, a dramatic enhancement of the linewidth was found as the critical point was approached. In other cases, no effect was detected even though measurements were carried into the range of  $10^{-4}$  or  $10^{-5}$  in  $\epsilon$ .

Very recently, a theory was developed which predicts a bounded critical contribution to the linewidth.<sup>1</sup> As the critical point is approached, both the magnitude of the density fluctuations in the fluid and their time scale increase. When both effects are taken into account, it is found that for values of  $\epsilon$  which are not too small, the linewidth will increase as  $\epsilon^{-0.6}$ . However, as  $\epsilon$  becomes sufficiently small, there is a cancellation of the critical contribution and the linewidth assumes a limiting value. We show that this theory can provide a simple criterion for the observation of a critical contribution to the linewidth. This criterion is found to qualitative-

ly account for the existing data on spectral line shapes near critical points.

The critical contribution to the linewidth reaches a maximum which is<sup>1,2</sup>

$$\hat{\Gamma}_c = A_0^{2/(3-\eta)} \tau_c^{-1}, \quad (1)$$

where  $\tau_c$  is a collision time,  $\eta$  is the Fisher-Burford exponent ( $\eta \cong 1/18$ ), and  $A_0$  is

$$A_0 = \langle U^2 \rangle \tau_c^2 \quad (2)$$

with  $\langle U^2 \rangle$  the mean-square fluctuation of the difference in the coupling to the surroundings of the two energy levels involved the spectral transition. Only the long wavelength part of the coupling is included in Eqs. (1) and (2), and so Eq. (2) is not necessarily derivable from the noncritical linewidth. However, we estimate  $\tau_c$  and  $\langle U^2 \rangle$  from noncritical parameters. We take  $\tau_c$  to be  $10^{-13}$  s<sup>3</sup> and take  $\langle U^2 \rangle$  from the shift of the center of the line  $\bar{\omega}$  with density  $\rho$ , under noncritical conditions, i.e.,

$$\langle U^2 \rangle = \left( \frac{\partial \bar{\omega}}{\partial \rho} \right)^2 \langle \Delta \rho^2 \rangle \ll \left( \frac{\partial \bar{\omega}}{\partial \rho} \right)^2 = \left( \frac{\partial \bar{\omega}}{\partial \ln \rho} \right)^2, \quad (3)$$

where  $\langle \Delta \rho^2 \rangle$  is the mean-square fluctuation in density and is obviously less than  $\rho^2$ . Although this estimate is crude, it has the advantage that the quantities on the right-hand side of the inequality are easily measured. Substituting Eqs. (2) and (3) into Eq. (1), we get the approximate relation

$$\hat{\Gamma}_c = \left( \frac{\partial \bar{\omega}}{\partial \ln \rho} \tau_c \right)^{(1+\eta)/(3-\eta)} \left( \frac{\partial \bar{\omega}}{\partial \ln \rho} \right). \quad (4)$$

TABLE I. Linewidths at critical points.

	$\rho \frac{\partial \bar{\omega}}{\partial \rho}, \text{ s}^{-1}$	$\left( \rho \frac{\partial \bar{\omega}}{\partial \rho} \tau_c \right)^{0.36}$	$\hat{\Gamma}_c \text{ s}^{-1}$	$\hat{\Gamma}_{nc} \text{ s}^{-1}$	Effect seen
N <sub>2</sub> <sup>a</sup>	$1.4 \times 10^{11}$	0.22	$0.31 \times 10^{11}$	$0.12 \times 10^{11}$	Y
O <sub>2</sub> <sup>a</sup>	1.7	0.23	0.39	0.22	Y
CH <sub>4</sub> <sup>a</sup>	7.8	0.40	3.1	4.8	Y
CO <sup>a</sup>	1.2	0.20	0.24	0.88	Y
CF <sub>4</sub> <sup>a</sup>	0.38	0.13	0.051	0.26	N
CO <sub>2</sub> <sup>b</sup> $\nu_1$	4.7	0.33	1.55	46 <sup>c</sup>	N
$2\nu_2$	2.4	0.26	0.63	46 <sup>c</sup>	N
C <sub>2</sub> H <sub>6</sub> <sup>d</sup>	0.83	0.18	0.15	2.2	N
Binary liquid <sup>e</sup>					
875 cm <sup>-1</sup> <sup>e</sup>	4.7	0.33	1.6	8.2	N
1100 cm <sup>-1</sup> <sup>e</sup>	9.4	0.43	4.0	17	N
445 cm <sup>-1</sup> <sup>e</sup>	8.5	0.41	3.5	19	N

<sup>a</sup> Reference 6.

<sup>b</sup> Reference 7. The two bands observed are part of a Fermi diad.

<sup>c</sup> This is the spectrometer slit width rather than the intrinsic width of the bands.

<sup>d</sup> Reference 5.

<sup>e</sup> Reference 8. The binary mixture is nitroethane (NE) and 3-methyl pentane (MP). The 875 and 1100 cm<sup>-1</sup> bands are of NE, the 445 cm<sup>-1</sup> band of MP.

The exponent  $(1 - \eta)/(3 - \eta)$  is about 0.36. Of course, this critical contribution will only be observable if  $\hat{\Gamma}_c$  is of the order of or greater than the noncritical contribution  $\hat{\Gamma}_{nc}$ . In Table I, we summarize the values of  $\hat{\Gamma}_c$  and  $\hat{\Gamma}_{nc}$  for the systems that have been studied experimentally. Note that a binary liquid mixture which has a critical point belonging to the same universality class as the gas-liquid point should exhibit the same behavior with the concentration  $C$  substituted for  $\rho$  in Eq. (4).

For the first four cases listed in Table I,  $N_2$ ,  $O_2$ ,  $CH_4$ , and  $CO$ ,  $\hat{\Gamma}_c$  is within a factor of 4 of  $\hat{\Gamma}_{nc}$  and the critical effect is observed. For the rest of the cases listed,  $\hat{\Gamma}_c$  is at least a factor of 4 smaller than  $\hat{\Gamma}_{nc}$  and no critical effect is observed. Our estimates of  $\hat{\Gamma}_c$  do rationalize the observations of the critical point effect. However, although our criterion  $\hat{\Gamma}_c/\hat{\Gamma}_{nc} > 0.25$  correctly predicts the observability of the effect, the apparent sharpness of the cutoff remains a bit of a mystery. The observations divide sharply into cases in which the critical effect is observed and cases in which it is not observed. The theory would suggest a continuous variation of the magnitude of the effect with  $\hat{\Gamma}_c$ . The success of this theory is all the more remarkable, because there are a number of different mechanisms that contribute to the line shifts and widths.<sup>5,6</sup>

It is worth noting the large range of both  $\hat{\Gamma}_c$  and  $\hat{\Gamma}_{nc}$  exhibited by the systems studied. Particularly striking are the 20-fold differences between  $CF_4$  and  $CH_4$  in both the

linewidth and the shift of line center with density.

Our results also suggest a method of planning future critical point experiments based on simple measurements of  $(\partial\bar{\omega}/\partial \ln \rho)$  away from the critical point. Finally, we note that the theory predicts that if the critical effect is observable at all, it will be observed starting at values of  $\epsilon$  which are not too small, say of the order of  $10^{-1}$ – $10^{-2}$  for the values of  $\hat{\Gamma}_c$  listed in Table I.

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<sup>1</sup>S. Mukamel, P. S. Stern, and D. Ronis, Phys. Rev. Lett. **50**, 590 (1983); Spectral Line Shapes **2**, 973 (1983).

<sup>2</sup>Some constants of the order of one have been omitted from Eqs. (1) and (2) (see Ref. 1). The  $\hat{\Gamma}$ 's are the full width at half-maximum in units of rad/s.

<sup>3</sup>The correlation time was calculated to be  $1.49 \times 10^{-13}$  s (Ref. 4) for liquid  $N_2$ . The Enskog collision time was estimated to be  $4.5 \times 10^{-13}$  s for ethane at its critical point (Ref. 5). The correlation times for all the other systems should be in the same range and we have taken them all as  $10^{-13}$  s for the purpose of calculation. See also Table I in Eq. (4a) for a list of collision times for other systems.

<sup>4</sup>(a) D. W. Oxtoby, Adv. Chem. Phys. **40**, 1 (1979); (b) D. W. Oxtoby, D. Levesque, and J. J. Weis, J. Chem. Phys. **68**, 5528 (1978).

<sup>5</sup>K. A. Wood and H. L. Strauss, J. Chem. Phys. **78**, 3455 (1983).

<sup>6</sup>M. J. Clouter, H. Kiefte, and R. K. Jain, J. Chem. Phys. **73**, 673 (1980).

<sup>7</sup>Y. Garrabos, R. Tufeu, B. LeNeindre, G. Zalczer, and D. Beysens, J. Chem. Phys. **72**, 4637 (1980).

<sup>8</sup>K. A. Wood and H. L. Strauss, J. Chem. Phys. **74**, 6027 (1981).

## COMMENTS

### Comment on: "Relativistic integrals over Breit-Pauli operators using general Cartesian Gaussian functions"

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In a recent paper by Chandra and Buenker<sup>1</sup> formulas for matrix elements over various terms of the Breit-Pauli Hamiltonian (BPH) in a Gaussian basis are presented. It is claimed that terms of higher order than  $p^4$  in the BPH are important and should be included in calculations for heavy atoms. It is further argued that ignoring these contributions may lead to serious inaccuracies. Numeric values of integrals over such terms are presented to support that claim. The aim of the present note is to show that the Taylor expansion of the BPH cannot be used as in Ref. 1 and, accordingly, that the conclusions cited above are unjustified. The relativistic field-free electron energy expression is given by

$$E = \sqrt{m^2c^4 + p^2c^2}. \quad (1)$$

As shown by Sucher,<sup>2</sup> Eq. (1) applies also to electrons in

an external field, provided that projection operators are introduced to restrict the wave function to purely electronic states. The square root in Eq. (1) is commonly expanded in a Taylor series

$$E = mc^2 + \frac{p^2}{2m} \sum_{k=0}^{\infty} \binom{2k}{k} \frac{1}{k+1} \left( \frac{-ip}{2mc} \right)^{2k} \quad (2)$$

which converges if  $p^2 < (mc)^2$ . For the operator analog of Eq. (2), it is necessary that the expansion converges for the entire spectrum of  $\hat{p}$ . For an operator with an unbounded spectrum this presents a problem which, however, may be circumvented by considering the projection into a suitably chosen subspace. In practical work on atoms this may be done by imposing additional constraints on the electron density close to the nucleus.<sup>3</sup> Unfortunately, with an arbitrary basis, e.g., a