

LINE BROADENING NEAR CRITICAL POINTS—A PROBE FOR DENSITY
FLUCTUATIONS

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The studies of critical phenomena have made a considerable progress in recent years. The introduction of scaling ideas and renormalization group techniques¹⁻³ have revealed the underlying universal features common to a variety of very different systems near critical points. Particular emphasis was made on calculating the critical exponents which characterize the behaviour of various quantities (correlation length, heat capacity, etc.) very close to the critical point. In this paper, we develop a microscopic theory for the broadening of an isolated spectral line near a liquid gas critical point. We derive a universal line shape function and analyze the critical exponent associated with the line width. We show how the line broadening serves as a probe for the dynamics of critical density fluctuations. Our analysis provides a quantitative explanation for the available

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experimental data on the vibrational dephasing linewidth in liquid nitrogen and oxygen⁴, together with a detailed prediction regarding the line shape function.

Consider a fluid consisting of N two-level particles with pairwise additive interactions. The ground state will be denoted $|a\rangle$ and the excited state $|b\rangle$. denoting the interaction of two atoms in the $|a\rangle$ state by $V_a(Q)$ and of one atom in $|a\rangle$ and another in $|b\rangle$ by $V_b(Q)$ then the interaction responsible for the line broadening is $U \equiv V_b(Q) - V_a(Q)$. Here, Q is the interatomic separation. The absorption line shape for this system $I(\Delta)$ may be written in the form⁽⁵⁾,

$$I(\Delta) = \frac{1}{\pi} \operatorname{Re} \int_0^{\infty} d\tau \exp(i\Delta\tau) \exp[-\phi(\tau)], \quad (1)$$

where

$$\phi(\tau) \equiv \int_0^{\tau} d\tau_1 (\tau - \tau_1) \langle U(\tau_1) U(0) \rangle. \quad (2)$$

Here $\Delta = \omega_L - \omega_{ba}$ is the detuning of the radiation frequency ω_L from the two-level frequency ω_{ba} and $\langle U(\tau) U(0) \rangle$ is the ground state correlation function:

$$\begin{aligned} \langle U(\tau) U(0) \rangle = & \sum_{\tilde{k}, \tilde{k}'} U_{\tilde{k}} U_{\tilde{k}'} [\langle \hat{N}_{\tilde{k}}(\tau) \hat{N}_{-\tilde{k}}(\tau) \hat{N}_{\tilde{k}'}(0) \hat{N}_{-\tilde{k}'}(0) \rangle \\ & - \langle \hat{N}_{\tilde{k}} \hat{N}_{-\tilde{k}} \rangle \langle \hat{N}_{\tilde{k}'} \hat{N}_{-\tilde{k}'} \rangle]. \end{aligned} \quad (3)$$

$N_{\underline{k}}$ and $\hat{N}_{\underline{k}}$ are the particle number density operators of the fluid and the density of a tagged particle (the absorber) respectively,

$$N_{\underline{k}} = \sum_{\alpha} \exp(i \underline{k} \cdot \underline{Q}_{\alpha}), \quad (4a)$$

$$\hat{N}_{\underline{k}} = \exp(i \underline{k} \cdot \underline{Q}_s), \quad (4b)$$

and

$$U_{\underline{k}} = \int d\underline{r} U(\underline{r}) \exp(i \underline{k} \cdot \underline{r}). \quad (4c)$$

Equation (3) holds for foreign broadening (the s particle is different from α) or for self broadening where s is identical with α , provided we neglect effects of resonance exchange of excitation. The evaluation of the line shape function (1) is now reduced to the calculation of the four point (three particle, two time) correlation function appearing in Eq. (3) and it is the critical behaviour of this correlation function that is being probed by the line broadening experiment.

Using standard correlation function manipulations, we may write:

$$\begin{aligned} \langle N_{\underline{k}}(\tau) \hat{N}_{-\underline{k}}(\tau) N_{\underline{k}} \hat{N}_{-\underline{k}} \rangle &\equiv \langle N_{\underline{k}} \hat{N}_{-\underline{k}} \rangle \langle N_{\underline{k}} \hat{N}_{-\underline{k}} \rangle \\ &+ \langle N_{\underline{k}}(\tau) N_{\underline{k}} \rangle \langle \hat{N}_{-\underline{k}}(\tau) \hat{N}_{-\underline{k}} \rangle + \langle N_{\underline{k}}(\tau) \hat{N}_{-\underline{k}} \rangle \langle \hat{N}_{-\underline{k}}(\tau) N_{\underline{k}} \rangle \quad (5) \\ &+ \langle \langle N_{\underline{k}}(\tau) \hat{N}_{-\underline{k}}(\tau) N_{\underline{k}} \hat{N}_{-\underline{k}} \rangle \rangle \equiv \text{I} + \text{II} + \text{III} + \text{IV} . \end{aligned}$$

Equation (5) is merely a definition of the cumulant average $\langle\langle\cdots\rangle\rangle$ defined as the difference of the four point correlation function and the three products obtained by factorizing it in all possible ways. It may be easily shown that the contribution to Eq. (3) of $\text{III}/\text{II} = O(1/\Omega)$, where Ω is the volume of the system. Thus in the thermodynamic limit ($\Omega \rightarrow \infty$, $N \rightarrow \infty$, $N/\Omega = n$ finite) we may safely ignore III. We have evaluated IV using mode coupling theory in the bare vertex approximation.^{6,7} This results in an expression for IV involving nonlinear couplings of N_k and \hat{N}_k to shear fluctuations. The shear relaxation time is much shorter than the time scales characterizing N_k (thermal diffusion) and \hat{N}_k (self diffusion). In addition, the shear viscosity is known not to display any strong critical behaviour.^{1,7} These two facts have allowed us to show that the contribution of IV/II is $O(\xi_0/\xi) \sim O((- \epsilon)^\nu)$, where ξ_0/ξ is the ratio of a microscopic length scale to the correlation length, $\epsilon = |T - T_c|/T_c$ is the reduced temperature and ν is the correlation length critical exponent. The actual calculation of IV is fairly involved and will be reported elsewhere.⁸

It must be stressed that IV is small only near the critical point. Away from T_c this need not be the case, i.e., IV small (and from our calculation seems to get quite large) and hence, the Gaussian approximation holds only near T_c . The term I is cancelled when (5) is substituted in (3). We therefore get:

$$\langle U(\tau)U(0) \rangle = U_0^2 \sum_{\tilde{k}} \langle N_{\tilde{k}}(\tau)N_{-\tilde{k}} \rangle \langle N_{-\tilde{k}}(\tau)\hat{N}_{\tilde{k}} \rangle. \quad (6)$$

In Eq. (6) we have also replaced U_k in the sum by U_0 since we are going to evaluate the sum in the long wavelength limit. We have evaluated Eq. (6) using the following hydrodynamic expressions for the two point correlation functions⁽¹⁾:

$$\langle \hat{N}_{-k}(\tau) \hat{N}_k \rangle = \exp(-D_S k^2 \tau), \quad (7a)$$

$$\frac{1}{\Omega} \langle N_k(\tau) N_{-k} \rangle = S(k) \exp(-D_T k^2 \tau). \quad (7b)$$

Here D_S is the self diffusion coefficient, D_T is the thermal diffusivity, $S(k)$ is the static structure factor and n is the number density in the fluid. A simple model for $S(k)$ is the Ornstein Zernike model^{1,9}:

$$S(k) = n \frac{\kappa_T}{\kappa_T^0} \frac{\kappa^2}{k^2 + \kappa^2} \quad (8)$$

Here κ_T/κ_T^0 is the ratio of the actual isothermal compressibility and that of an ideal gas and $\kappa = \xi^{-1}$ is the inverse of the correlation length which vanishes at the critical point. Upon substitution of Eqs. (7) and (8) in Eq. (6) and switching the k summation to integration

$$\sum_{\tilde{k}} + \frac{\Omega}{(2\pi)^3} \int d\tilde{k} \quad (9)$$

we finally get:

$$\phi(\tau) = A \cdot F(\Gamma \kappa^2 \tau), \quad (10)$$

where

$$A = \frac{1}{4\pi} \frac{\kappa_T}{\kappa_0} \frac{U_0 n}{\Gamma^2 \kappa} \quad (10a)$$

$$F(x) = x + 1 - \exp(x) \operatorname{erfc}(\sqrt{x}) - 2\sqrt{x/\pi} \quad (10b)$$

and

$$\Gamma = D_S + D_T \quad (10c)$$

The function $F(x)$ behaves as $-x^{3/2}$ for $x \ll 1$, and asymptotically for $x \gg 1$, $F \sim x$. A simple uniform approximation for $F(x)$ (good to within $\sim 5\%$) is:

$$F(x) = \frac{\frac{4}{3\sqrt{\pi}} x^{3/2}}{1 + \frac{4}{3\sqrt{\pi}} x^{1/2}} = \frac{0.752 x^{3/2}}{1 + 0.752 x^{1/2}} \quad (11)$$

Consequently, we have:

$$\exp[-\phi(\tau)] \sim \begin{cases} \exp(-A\Gamma\kappa^2\tau) & , A \lesssim 10^{-2} \\ \exp\left[-\frac{4}{3\sqrt{\pi}} (A^2/3\Gamma\kappa^2\tau)^{3/2}\right] & , A \gtrsim 10^2 \end{cases} \quad (12)$$

Therefore for small A , $A \ll 10^{-2}$ the line shape assumes a Lorentzian form with full width at half maximum $\hat{\Gamma} = 2A\Gamma\kappa^2$. For $A \gg 10^2$ the line assumes the form of a Levy distribution⁽¹⁰⁾ with the width $\hat{\Gamma} \sim A^{2/3}\Gamma\kappa^2$.

A more realistic expression for $S(k)$ is the Fisher Burford Approximant, i.e.:

$$S(k) = n \frac{\kappa_T}{\kappa_0} \frac{(1 + \Psi 2k^2/\kappa^2)^{n/2}}{1 + (1 + \Psi 2\eta/2)k^2/\kappa^2} \quad (13)$$

Here $\Psi = 0.075$ and $\eta = 1/18$ is the Fisher Burford exponent.¹¹ When $\Psi = \eta = 0$, Eq. (13) reduces to the Ornstein Zernike form, (Eq. (8)). The significance of η is as follows: At the critical temperature $T = T_c$ then $\kappa = 0$ and

$$S(k) \sim k^{-2+\eta} \quad (14a)$$

Therefore the density correlation function

$$G(\underline{r}) = \int d\underline{k} S(k) \exp(i\underline{k} \cdot \underline{r})$$

$$\xrightarrow{r \rightarrow \infty} r^{-(1+\eta)} \quad (14b)$$

η therefore characterizes the power law decay of $G(\underline{r})$ at T_c . Using Eqs. (7), (13), and (6), we finally get that Eq. (10) still holds in this case but $F(x)$ is given by the following integral which should be evaluated numerically:

$$F(x) = \frac{\sqrt{x}}{\pi} \int_0^{\infty} dy \frac{(1 + \Psi y/x)^{n/2}}{1 + (1 + \Psi \eta/2)y/x} \frac{\exp(-y) + y^{-1}}{y^{3/2}} \quad (15)$$

A plot of $F(x)$ is shown in Figure 1.

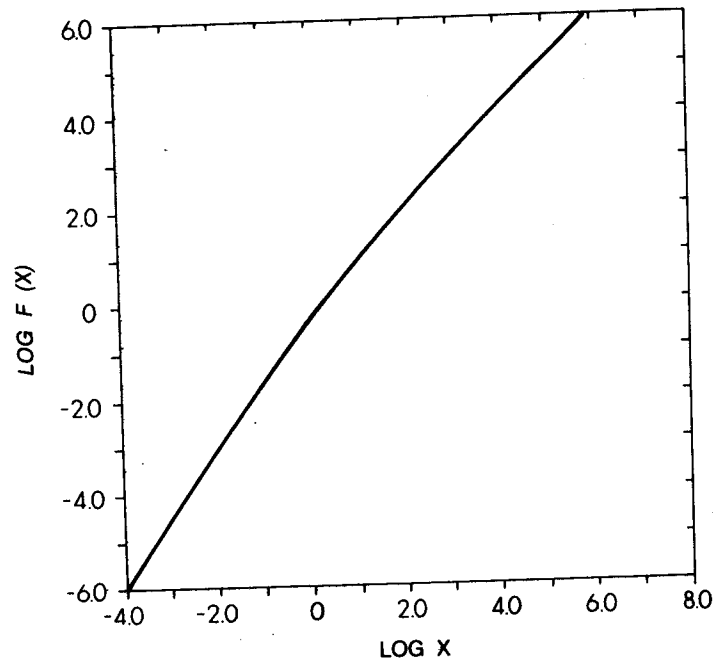


FIGURE 1

$\text{Log}_{10} F(x)$ versus $\text{log}_{10} x$ for the Fisher Burford model (Eq. 15). Note that the slope gradually changes from $(3-n)/2$ for $x \ll 1$ to 1 for $x \gg 1$.

The function $F(x)$ behaves as $x^{(3-\eta)/2}$ for $x \ll 1$, and asymptotically for $x \gg 1$, $F \sim x$. A simple uniform approximation for $F(x)$ is:

$$F(x) \cong \frac{0.715x^{(3-\eta)/2}}{1 + 0.706x^{(1-\eta)/2}} \quad (16)$$

consequently we have:

$$\exp(-\phi(\tau)) \cong \begin{cases} \exp(-A\Gamma\kappa^2\tau) & , A < 10^{-2} \\ \exp[-0.7(\Gamma\kappa^2\tau)^{(3-\eta)/2}] & , A > 10^2 \end{cases} \quad (17)$$

Therefore for small A , $A < 10^{-2}$ the line shape assumes a Lorentzian form with full width at half maximum $\hat{\Gamma} = 2A\Gamma\kappa^2$. For $A > 10^2$, the line assumes the form of a Levy distribution¹⁰ with the width $\hat{\Gamma} = (A)^{2/(3-\eta)}\Gamma\kappa^2$. In Figure 2 we show a few line shapes obtained using Eqs. (1), (10) and (15) and in Figure 3 we display $\log \hat{\Gamma}$ vs. $\log A$. We note that as predicted from the above analysis the slope of the curve changes from 1 for $A < 10^{-2}$ to $2/(3-\eta)$ for $A > 10^2$. We are now in a position to analyze the critical behaviour of our line shape. To that end let us recall the critical behaviour of the various parameters which appear in Eq. (10):

$$\kappa = \kappa_0 \varepsilon^\nu, \quad (18a)$$

$$\frac{\kappa_T}{\kappa_0} \approx \frac{4}{9} \varepsilon^{-\gamma}, \quad \text{where the factor of } 4/9 \text{ is obtained from} \quad (18b)$$

the Van Der Waals equation of state,

$$D_S \approx \frac{kT\kappa_0}{6\pi\bar{\eta}} \sim \epsilon^0, \tag{18c}$$

$$D_T \approx \frac{kT\kappa}{6\pi\bar{\eta}} \sim \epsilon^\nu, \tag{18d}$$

Here κ_0 is a microscopic wave vector $\sim 1A^{-1}$ and $\bar{\eta}$ is the viscosity. The critical exponents ν and γ are $\nu = 9/14$ and $\gamma = 1.25$.

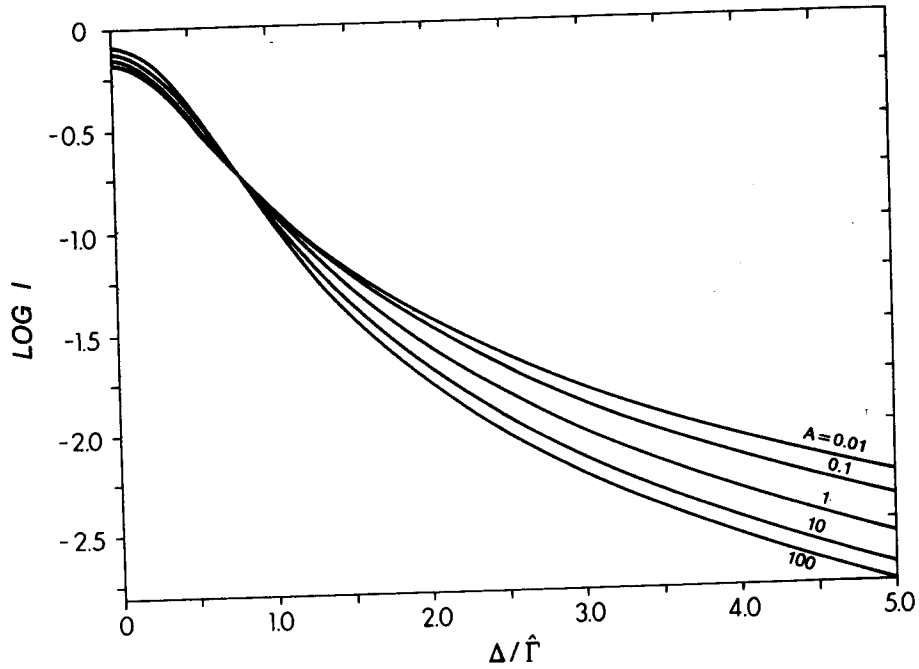


FIGURE 2

The line shape function (Eqs. (1), (10), and (15)) for various values of A . The detuning Δ is scaled by the full width half maximum $\hat{\Gamma}$ in each case.

Using Eqs. (10) and (18) we get the critical behaviour of our line shape parameters:

$$A = A_0 \varepsilon^{-\gamma-\nu}, \quad (19a)$$

$$A_0 = \frac{1}{9\pi} \frac{U_{0n}^2}{\Gamma^2 \kappa_0}, \quad (19b)$$

$$\Gamma = D_T + D_S \sim \varepsilon^0. \quad (19c)$$

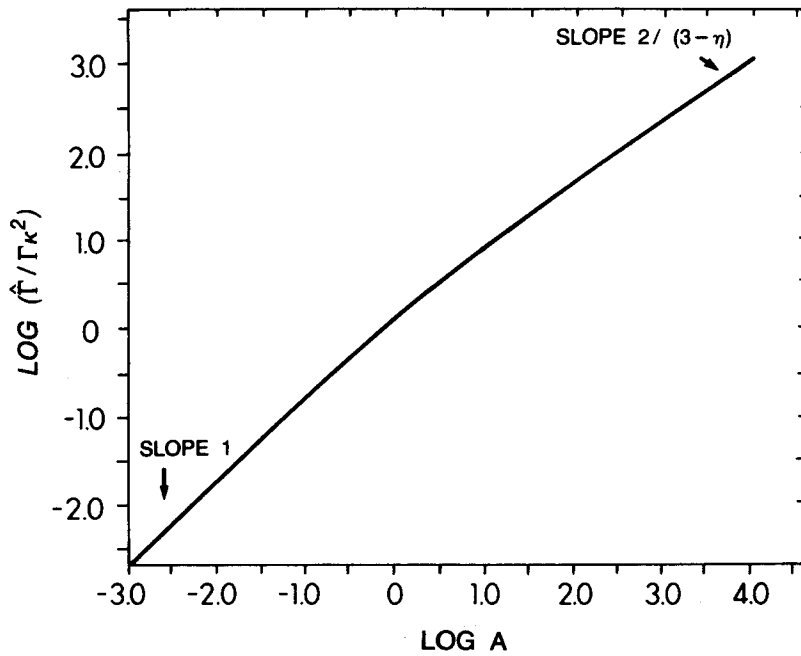


FIGURE 3

The universal behaviour of the dimensionless linewidth ($\hat{f}/\Gamma\kappa^2$) vs. A . Note how the slope gradually changes from 1 for small A to $2/(3-\eta)$ for large A .

Using Eqs. (17) and (19) we immediately get for the full width at half maximum FWHM, $\hat{\Gamma}$ of our line shape function:

$$\hat{\Gamma} = \epsilon^s \quad (20)$$

$$s = \begin{cases} -\gamma + \nu = -0.607 & A \lesssim 10^{-2} \\ -2[\gamma - \nu(2-n)]/(3-n) = 0 & A \gtrsim 10^2 \end{cases} \quad (20a)$$

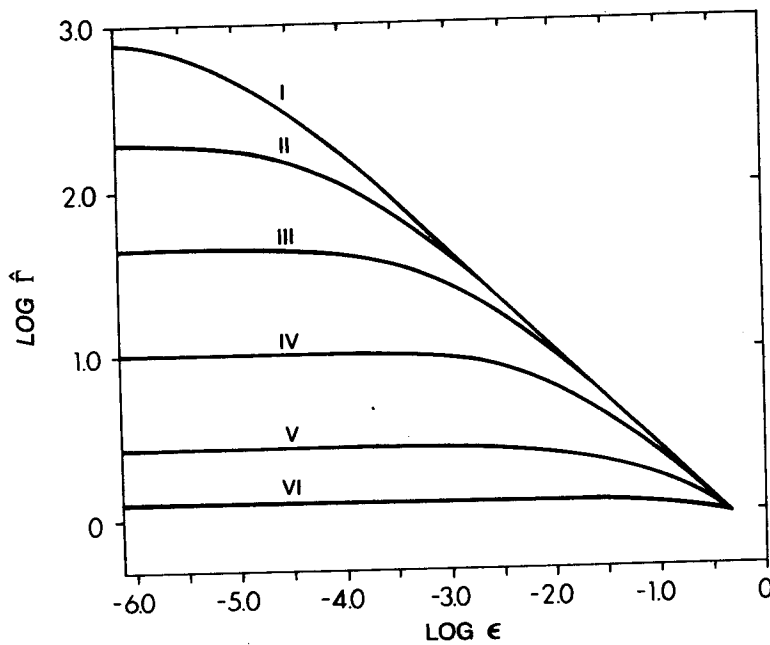


FIGURE 4

The linewidth $\hat{\Gamma}$ vs. ϵ for various values of A_0 . In all cases the slope changes from -0.607 for large ϵ to 0 for small ϵ . Curves I-VI correspond to $A_0 = 2.5 \times 10^{-10}$, 2.5×10^{-8} , 2.5×10^{-6} , 2.5×10^{-4} , 2.5×10^{-2} and 2.5 respectively. Eqs. (1), (10) and (15) were used in the calculation.

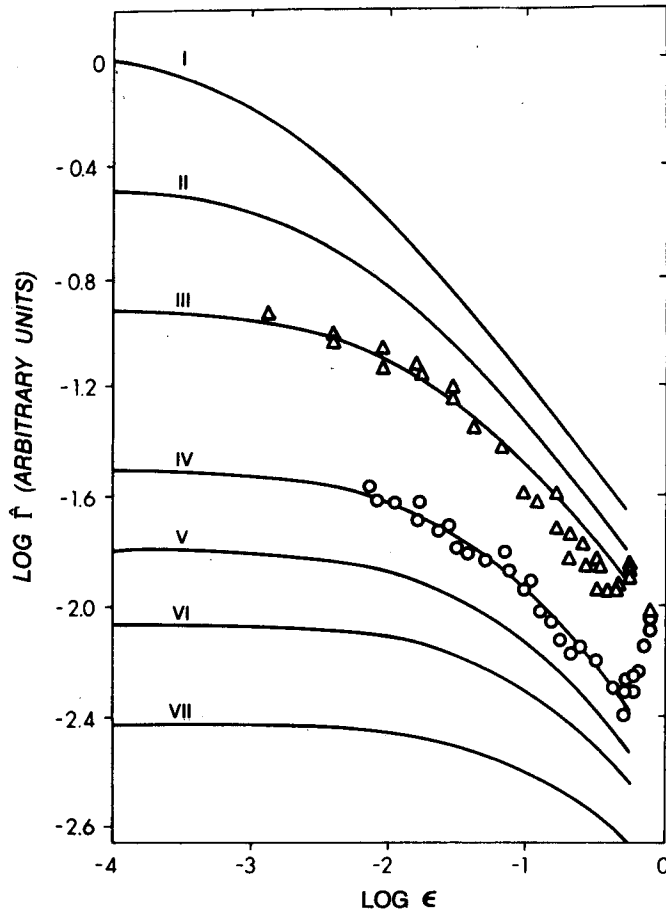


FIGURE 5

The fit of our theory (Eqs. (1), (10) and (15)) to experiment. The various curves were shifted arbitrarily in the vertical direction for the clarity in the presentation. The points are the experimental data of Clouter and Kiefte(4) on vibrational Raman linewidth in O_2 (O) and N_2 (Δ).

$$I - A_0 = 2.5 \cdot 10^{-6}, \quad II - A_0 = 2.5 \cdot 10^{-5}, \quad III - A_0 = 2.5 \cdot 10^{-4}$$

$$IV - A_0 = 7.5 \cdot 10^{-4}, \quad V - A_0 = 2.5 \cdot 10^{-3}, \quad VI - A_0 = 7.5 \cdot 10^{-3}$$

$$VII - A_0 = 2.5 \cdot 10^{-2}$$

In Eq. (20), we have assumed that we are close enough to the critical point so that $D_T \ll D_S$. Should the reverse be true, then $\Gamma \sim \epsilon^\nu$ and the slope s in the $A \ll 10^{-2}$ case will change to $s = -\gamma = -1.25$. The vanishing of s for $A \gg 10^2$ arises from the scaling identity $\gamma = \nu(2-\eta)$. In Figure 4, we display $\log \hat{\Gamma}$ vs. $\log \epsilon$ for various values of A_0 . All the information necessary for Figure 4 is contained in Figure 3 together with Eq. (12a). We note that the slope gradually changes from -0.607 to 0 but the value of ϵ for which the crossover occurs depends on the value of A_0 . The experimental data⁴ for O_2 and N_2 are displayed in Figure 5 and the fit is very good with $A_0 = 7.5 \cdot 10^{-4}$ and $2.5 \cdot 10^{-4}$ respectively. The value of A_0 obtained here agrees very nicely with the ordinary (non critical) data for liquid N_2 ¹². We note that away from the critical point $\tau_c = (\Gamma \kappa_0^2)^{-1}$ is a duration of collision and $\langle U^2 \rangle = U_0^2 n / \kappa_0^3$ is the ensemble average for U_0 (n / κ_0^3 is the mean number of perturbers in the interaction region and U_0^2 is the interaction per perturber). We therefore have $A_0 \sim \langle U^2 \rangle \tau_c^2$. The latter quantity was evaluated by Oxtoby¹² for liquid N_2 and found to be $\sim 10^{-3}$ which is in a reasonable agreement with our fit.

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