TABLE I. Values of E_M (unit: $Z^2 e^2/a_0$).

M	E_M^{exact}	E_M (Ref. 4)	$\overline{E}_M$	E_M^{TF}
1	-0.5000	-0.5280	-0.6349	-0.7211
5	-1.0000	-1.0541	-1.1825	-1.2331

$$\langle \frac{p^2}{2m} \rangle_M = -\frac{1}{2} \langle \frac{Ze^2}{r} \rangle_M = -\overline{E}_M.$$

That is, the virial theorem is satisfied by the expectation values of the original kinetic-energy and potential-energy operators. In fact, $\overline{E}_M$ may be approximated by

$$\overline{E}_M \doteq \left(-\frac{(3M)^{1/3}}{2} + \frac{1}{8(3M)^{1/3}} - O(M^{-5/3}) \right) \left(\frac{Z^2 e^2}{a_0} \right),$$

$$M \gg \frac{1}{12}. \qquad (3.23)$$

This is to be compared with the exact and the Thomas-Fermi results

$$E_M^{\text{exact}} \doteq \left(-\frac{(3M)^{1/3}}{2} + \frac{1}{4} - \frac{1}{24(3M)^{1/3}} + O(M^{-5/3}) \right)$$

$$\times \left(\frac{Z^2 e^2}{a_0} \right), \qquad M \gg \frac{1}{36\sqrt{3}} \qquad (3.24)$$

$$E_M^{\text{TF}} = -\frac{(3M)^{1/3}}{2} \left(\frac{Z^2 e^2}{a_0} \right). \qquad (3.25)$$

Since both Eqs. (3.23) and (3.24) are quite accurate even for $M = 1$ (we find $\overline{E}_1 \doteq -0.6344$ and $E_1^{\text{exact}} \doteq -0.5000$), we may conclude from Eqs. (3.23)–(3.25) that

$$E_M^{\text{exact}} > \overline{E}_M > E_M^{\text{TF}} \quad \text{all } M \text{ (closed shells)}. \qquad (3.26)$$

The radial density $\overline{R}_M(\eta)$, for which

$$\overline{R}_M(\eta)\, d\eta = 4\pi r^2 \overline{\rho}_M(r)\, dr, \quad \eta = Zr/a_0,$$

may be derived from Eqs. (3.12) and (3.14). It is

$$\overline{R}_M(\eta) = \frac{2}{3\pi} \left(\frac{2}{1 - \alpha_B} \right)^{3/2} \eta^2 \left(\frac{\eta - \alpha_B/8}{\eta^2} - 2\alpha_B \right)^{3/2},$$

$$\eta_2 \gtrsim \eta \gtrsim \eta_1 \qquad (3.27)$$

where

$$\eta_{1,2} = \frac{1}{4\alpha_B} [1 \pm (1 - \alpha_B^2)^{1/2}].$$

$\overline{R}_1(\eta)$ is found to be very similar to that obtained in Ref. 4. The cutoff points are, respectively, $\eta_1 = 0.0169$ and $\eta_2 = 3.7081$.

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Explanation of a Transient Raman Gain Anomaly

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By adding a small amount of absorption to many liquids, it is shown that the stimulated Raman emission and self-phase modulated emission pulse trains are radically shortened from that of a long pulse train of a mode-locked picosecond laser. The first pulses in a picosecond pulse train are more efficient in producing self-focusing because of self-absorption.

Self-heating effects cause defocusing which affect the efficiency of stimulated Raman scattering (SRS) and self-phase modulation (SPM) processes. This thermal defocusing explains the puzzle observed by Carman et al.[1] and Colles.[2] That puzzle was that only the leading pulses in a long picosecond
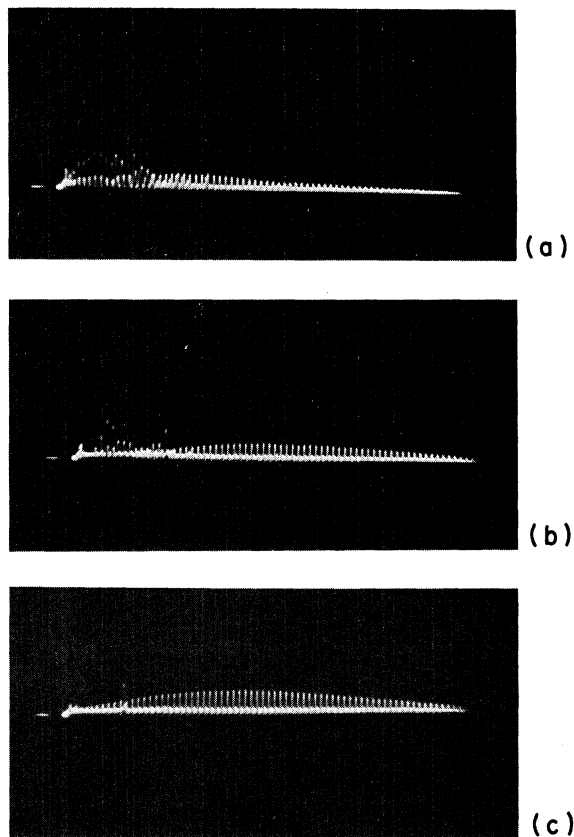
FIG. 1. SRS pulses interleaved with laser pulses: (a) Pure methanol, (b) absorption $= 34 \times 10^{-4}$ cm^{-1}, (c) absorption $= 138 \times 10^{-4}$ cm^{-1}. Laser pulses spaced by 5 nsec.

that heating effects are responsible for shortening the SRS plus SPM train, a dye absorber (7-diethyl-amino-4-dimethyl coumarin) is added to methanol, benzene, carbon disulfide, and carbon tetrachloride. The absorption at 5300 Å is varied from 5×10^{-4} cm^{-1} up to 140×10^{-4} cm^{-1} in these liquids by changing the coumarin concentration. The number of pulses in the SRS plus SPM train is examined as a function of absorption.

Figure 1 shows typical SRS pulse trains from methanol interleaved with the laser pulse train. The SRS train occurs at the beginning of the laser pulse train. As coumarin absorption is added to the sample, the Raman pulse train shortens. Figure 1(c) shows one intense Raman pulse. In Fig. 2, SPM trains from carbon disulfide are presented. Figure 2(a) shows the trains for the pure liquid, while Figs. 2(b)–2(d) show the effect of coumarin absorption and also the intensity dependence on the efficiency of SPM processes. Notice in Fig. 2(d) how the laser train at first is weak, and as it suddenly increases in intensity, the Raman train increases and then very abruptly disappears. Figure 3 shows how the typical number of pulses in the SRS and SPM train varies with coumarin absorption of light in benzene, carbon tetrachloride, carbon disulfide, and methanol. Each data point represents approximately ten laser shots. The laser fluctuates by approximately a factor of 2 in power.
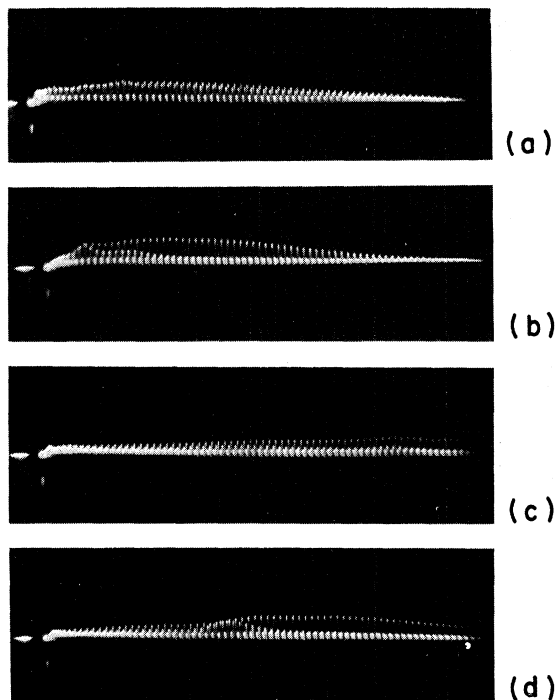
pulse train were effective in SRS. The slight absorption present in pure liquids is sufficient to shorten the SRS train. With the addition of small amounts of an absorber, the SRS train becomes still shorter. This is because the first pulses in the train heat the liquid leading to a gradient in refractive index that tends to counteract the self-focusing of the latter pulses in the train.

A 5300-Å picosecond pulse train of approximately 60–70 pulses of peak power 0.5 GW per pulse is focused with a 20-cm focal-length lens into liquid samples 20 cm long. The beam waist length is approximately 7 cm long with a beam waist diameter of 350 μm. A beam splitter before the sample reflects the laser train through a 2-61 filter, reducing the laser intensity by a factor of 100, and then into a TRG 105B phototube; a mirror after the sample reflects the beam through 3-67 and 3-68 filters, allowing the SRS and SPM train into the same phototube. The SRS and SPM train is delayed relative to the laser train by approximately half the cavity transit time so that laser and Raman trains become interleaved. The signals are displayed on a Tektronix 519 scope. In order to show

FIG. 2. SPM pulses interlaced with laser pulses: (a) Pure carbon disulfide, (b)–(d) absorption $= 62 \times 10^{-4}$ cm^{-1}.
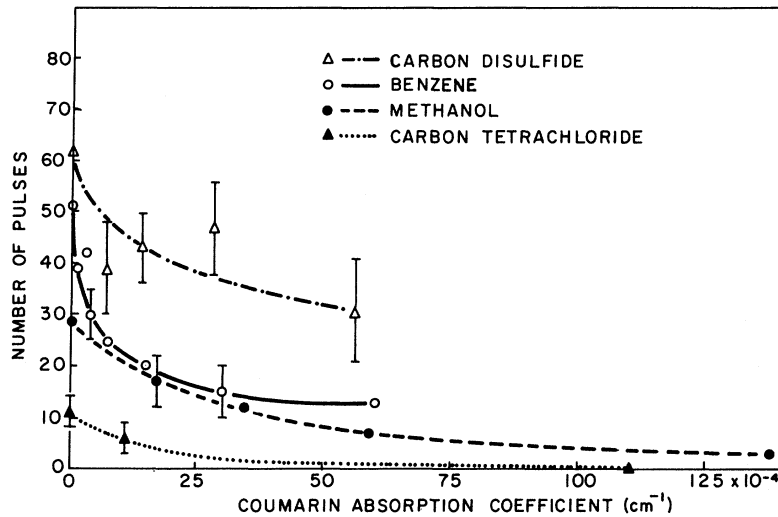
FIG. 3. Number of SPM and SRS pulses versus coumarin absorption . Solid line: benzene; dot-dashed line: carbon disulfide; dashed line: methanol; dotted line: carbon tetrachloride.

In pure carbon disulfide, the SPM train follows the laser train, pulse for pulse. A very large absorption, 60×10^{-4} cm^{-1} , is needed before the SPM train decreases in length to about half that of the laser pulse train. In pure benzene, a slight absorption of 6×10^{-4} cm^{-1} is sufficient to decrease the SPM plus SRS pulse train by a factor of 2, while in methanol the absorption of the pure liquid is sufficient to decrease the SRS pulse train approximately by 2. Carbon tetrachloride, which is known to have a small Kerr constant, is unable to counteract the defocusing effect caused by self-heating.

To explain these results, we write the refractive index of the material as

$$n = n_0 + n_2 E^2 + n_{2h} E^2 \quad , \quad (1)$$

where n_0 is the refractive index, $n_2 E^2$ is the nonlinear focusing term which in our case is due to the Kerr effect, and $n_{2h} E^2$ takes into account the change in refractive index due to the heat caused by absorption of the laser. Here $n_{2h} E^2$ is given by $(dn/dT)\Delta T$, where T is the temperature. The term $n_{2h} E^2$ is usually negative since the derivative of the refractive index with respect to temperature is usually negative,[3] although in lead glass[4] and semiconductors[5] it can be positive.

An estimate of n_{2h} resulting from heating effects in a pure liquid can be made from Leite et al.[6] For a typical pure-liquid absorption of 5×10^{-4} cm^{-1}, we estimate a change in temperature in our liquids of $\sim 10^{-3}$ °K per pulse, taking $C_V = 1.2$ J/cm^3 °K,

dn/dT as 5×10^{-4}/°K, and the length of the beam waist of 7 cm and 3 mJ per pulse. For this absorption, the change in refractive index for thirty pulses is 0.15×10^{-4}. For a coumarin absorption 10 times as great, the index change would be 1.5×10^{-4} after 30 pulses. This index change is comparable with the nonlinear term $n_2 E^2$ which in our case is $\sim 10^{-4}$. The defocusing due to thermal heating explains the shorter pulse trains observed by Carman et al.,[1] who inferred the existence of an unknown transient effect. Colles[2] noted that SRS conversion in nitrobenzene which absorbs at 5300 Å was anomalously low. Clearly, our results suggest that heating plays a role in suppressing SRS in nitrobenzene. The defocusing also explains the shorter self-phase modulated pulse trains observed in liquids and crystals.[7] The reason more SRS and SPM pulses are observed in benzene and carbon disulfide than the other liquids for the same coumarin aborption must be because the Kerr-effect term $n_2 E^2$ is much stronger in benzene and carbon disulfide, and therefore it dominates the defocusing term.

Absorption of individual light pulses takes place at constant volume, and then the medium expands at a rate determined by the acoustic phonon velocity. Thus it takes approximately 5–10 laser pulses (25–50 nsec) to develop a large defocusing refractive index gradient.

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Density and Compressibility of Oxygen in the Critical Region*

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Density-versus-height profiles have been measured in the critical region of oxygen by means of capacitance techniques. Results are given for the liquid and vapor densities at coexistence, for compressibilities along the coexistence curve to within $t \equiv (T - T_c)/T_c = -6 \times 10^{-5}$, for compressibilities along the critical isotherm to within $(\rho - \rho_c)/\rho_c = 5 \times 10^{-2}$, and for compressibilities along the critical isochore to within $t = 2 \times 10^{-4}$. The data are analyzed in terms of power-law descriptions and are shown to be in excellent agreement with recent scaling-law analyses of data for other fluids.

I. INTRODUCTION

The behavior of fluids in the critical region is generally described by power laws, which are expected to hold in the limit as the critical point is approached. Experimental data are analyzed in terms of a set of coefficients and exponents in the following relationships[1]: for $\rho = \rho_c$, $T > T_c$,

$$\rho_c^2 K_T = \Gamma t^{-\gamma} , \tag{1}$$

$$C_v = A t^{-\alpha} ; \tag{2}$$

for $\rho = \rho_c$, $T < T_c$,

$$C_v = A(-t)^{-\alpha'}; \tag{3}$$

for $T = T_c$,

$$p(\rho, T_c) - p(\rho_c, T_c) \sim \mu(\rho, T_c) - \mu(\rho_c, T_c) = D \Delta\rho |\Delta\rho|^{\delta-1}; \tag{4}$$

coexistence curve,

$$\Delta\rho = B(-t)^\beta, \tag{5}$$

$$\rho^2 K_T = \Gamma'(-t)^{-\gamma'}, \tag{6}$$

where $\Delta\rho = (\rho - \rho_c)/\rho_c$, $t = (T - T_c)/T_c$, K_T is the isothermal compressibility, and μ is the chemical potential.

The failure of the classical, or mean-field, theories to yield the correct values for the exponents and coefficients in the above equations has

been demonstrated many times experimentally. Calculations based on the Ising model, or its lattice-gas analog, agree more closely with the existing body of experimental evidence although significant differences still exist.

The scaling-law equation of state, proposed by Widom,[2] Griffiths,[3] Kadanoff,[4] and others, is a more phenomenological approach. It offers promise of giving a formulation of the thermodynamic behavior in the critical region which would be in good agreement with the most reliable data available. This equation may be expressed in the following form:

$$\mu(\rho, T) - \mu(\rho_c, T) = \Delta\rho |\Delta\rho|^{\delta-1} h(x), \tag{7}$$

with $h(x)$ being a function only of the variable $x = t/|\Delta\rho|^{1/\beta}$, and $x = -x_0$, a constant, on the coexistence boundary. Vicentini-Missoni, Sengers, and Green[5] have applied this equation of state to the experimental data on CO_2, Xe, and He[4] with good success. However, they cite the need for new data and consider their conclusions tentative because of the lack of extensive, precise experimental information.

Equation (7) implies several assumptions about the symmetry of the PVT surface in the critical region. Some of these are the following: (a) $\Delta\mu = \mu(\rho, T) - \mu(\rho_c, T)$ is antisymmetric about ρ_c and (b) $\gamma = \gamma' = \beta(\delta - 1)$. Calculations based on the three-
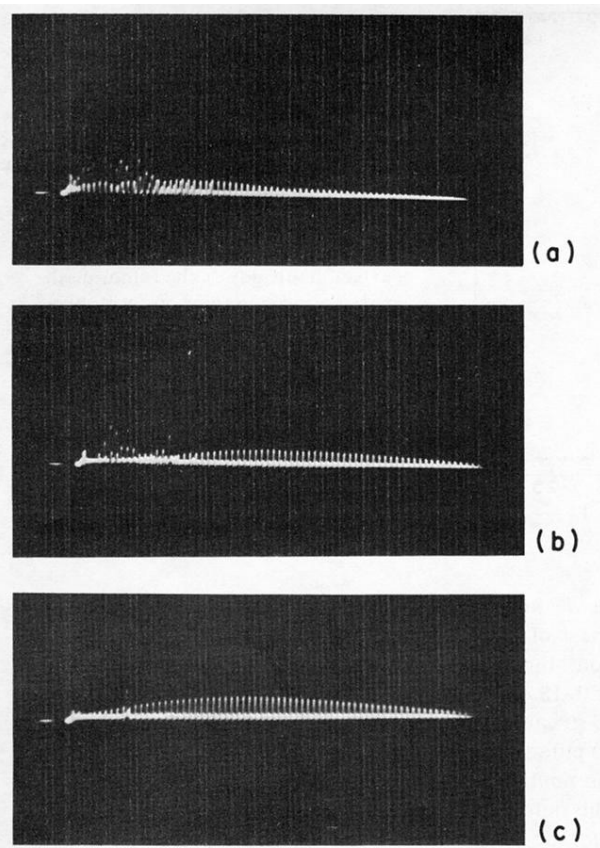
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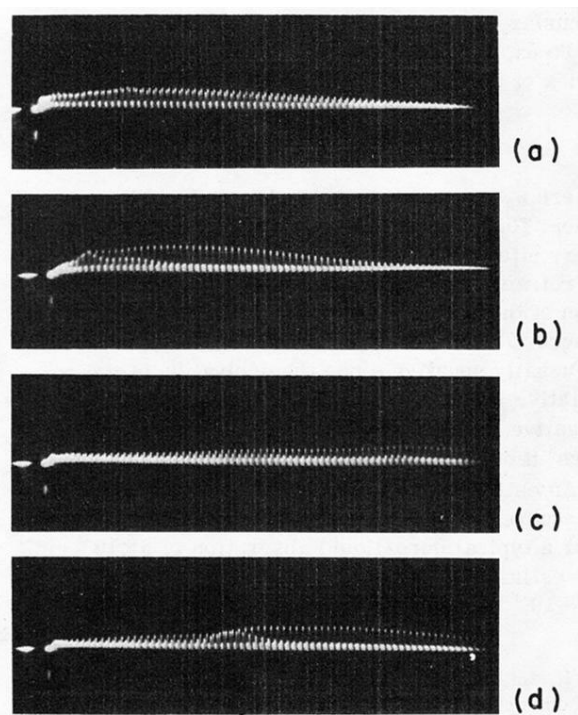
FIG. 2. SPM pulses interlaced with laser pulses: (a) Pure carbon disulfide, (b)−(d) absorption = 62×10^{-4} cm^{-1}.