

[†]Work supported in part by the Robert A. Welch Foundation and in part by the U. S. Atomic Energy Commission.

¹P. Richard, I. L. Morgan, T. Furuta, and D. Burch, *Phys. Rev. Lett.* **23**, 1009 (1969); D. Burch and P. Richard, *Phys. Rev. Lett.* **25**, 983 (1970).

²P. H. Mokler, *Phys. Rev. Lett.* **26**, 811 (1970); S. Datz, C. D. Moak, B. R. Appleton, and T. A. Carlson, *Phys. Rev. Lett.* **27**, 363 (1971); D. Burch and P. Richard, *Bull. Am. Phys. Soc.* **16**, 74 (1971); H. Kamada, T. Tamura, and M. Teresawa (unpublished).

³A. R. Knudson, D. J. Nagel, P. G. Burkhalter, and K. L. Dunning, *Phys. Rev. Lett.* **26**, 1149 (1971); D. Burch, P. Richard, and R. L. Blake, *Phys. Rev. Lett.* **26**, 100 (1971); D. G. McCrary and P. Richard, *Phys. Rev. A* **5**, 1249 (1972).

⁴P. G. Burkhalter, A. R. Knudson, and D. J. Nagel, *Bull. Am. Phys. Soc.* **17**, 500 (1972).

⁵R. C. Der, R. J. Fortner, T. M. Kavanagh, J. M. Khan, and J. D. Garcia, *Phys. Lett.* **36A**, 239 (1971).

⁶U. Fano and W. Lichten, *Phys. Rev. Lett.* **14**, 627 (1965).

⁷M. Barat and W. Lichten, *Phys. Rev. A* **6**, 211 (1972).

⁸D. Burch, in International Conference on Inner-Shell Ionization, Atlanta, Ga., 1972 (unpublished).

⁹J. M. Hansteen and O. P. Mosebekk, *Phys. Rev. Lett.* **29**, 1361 (1972).

¹⁰A. R. Knudson, P. G. Burkhalter, and D. J. Nagel, in International Conference on Inner-Shell Ionization, Atlanta, Ga., 1972 (unpublished); S. Hansen, J. H. McGuire, and R. L. Watson (to be published); M. J. Saltmarsh, A. van der Woude, and C. A. Ludemann, *Phys. Rev. Lett.* **29**, 392 (1972); J. H. McGuire and M. H. Mittleman, *Phys. Rev. A* **5**, 1971 (1972); R. L. Kauffman, C. F. Moore, P. Richard, and J. H. McGuire, C. F. Moore, D. K. Olsen, and R. L. Kauffman (unpublished).

¹¹J. A. Bearden, *Rev. Mod. Phys.* **31**, 1 (1967).

¹²F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Englewood Cliffs, N. J., 1963).

¹³J. D. Garcia, *Phys. Rev. A* **1**, 280 (1970).

¹⁴M. Gryzinski, *Phys. Rev.* **138**, A336 (1965).

¹⁵J. Bang and J. M. Hansteen, *K. Dan. Vidensk. Selsk. Mat.-Fys. Medd.* **31**, No. 13 (1959).

¹⁶E. Merzbacher and H. W. Lewis, in *Encyclopedia of Physics*, edited by S. Flügge (Springer-Verlag, Berlin, 1958), Vol. 34, p. 166.

¹⁷F. P. Larkins, *J. Phys. B* **4**, L29 (1971).

Electrocaloric Effect in Fluids and Its Relationship with Nonlinear Light Scattering*

K. H. Wang[†] and R. M. Herman

The Pennsylvania State University, University Park, Pennsylvania 16802

(Received 20 November 1972)

We derive an equation describing the electrocaloric effect in fluids, which differs from that predominantly employed in current theoretical studies of nonlinear optics. The consequent alterations in the predictions of nonlinear optical theory and in the interpretation of experimental observations are then described.

I. INTRODUCTION

In recent years, stimulated light scattering from isobaric temperature (entropy) excitations in liquids has acquired importance by itself, as well as in conjunction with other scattering mechanisms.¹⁻³ The first reported observation of stimulated thermal scattering (STS) was that of Rank, Cho, Foltz, and Wiggins⁴ following the theoretical description by Herman and Gray⁵ who indicated the importance of the absorptive heating mechanism in light scattering. (We call this phenomenon STS-II, in conformity with current practice.) Almost simultaneously, Zaitzev, Kyzylasov, Starunov, and Fabelinski⁶ reported the discovery of a scattering phenomenon in benzene and methanol which they attributed to the generation of entropy waves through the electrocaloric effect (STS-I). Following this, Mash *et al.*⁷ observed a scattering in gaseous H₂ which they also attributed to the electrocaloric coupling.

In the literature which has followed, however, there has not been complete agreement on the form

for the electrocaloric coupling leading to STS-I. Most investigators^{1,3,6-9} appear to have used equations describing the energy balance in fluids of the form

$$\rho C_v \frac{\partial T}{\partial t} - \frac{(\gamma - 1)C_v}{\beta} \frac{\partial \rho}{\partial t} = \dot{Q} + \lambda \nabla^2 T, \quad (1)$$

with

$$\dot{Q} = -\frac{1}{8\pi} T_0 \left(\frac{\partial \epsilon}{\partial T} \right)_p \frac{\partial E^2}{\partial t}, \quad (2)$$

while others^{10,11} have employed Eq. (1) with \dot{Q} given, instead, by

$$\dot{Q} = -\frac{1}{8\pi} T_0 \left(\frac{\partial \epsilon}{\partial T} \right)_p \frac{\partial E^2}{\partial t}. \quad (3)$$

In still another treatment,² Eq. (3) is taken to be valid and then, without elaboration, the authors allow that it is acceptable to employ Eq. (2) when describing STS-I.

The notation in these equations is standard, ρ and T being density and pressure variations from the corresponding equilibrium values ρ_0 and T_0 ,

and \dot{Q} representing an effective rate of heat input per unit volume due to the electrocaloric effect. The derivatives of the dielectric constant with temperature at constant pressure and density are given by $(\partial\epsilon/\partial T)_\rho$ and $(\partial\epsilon/\partial T)_\rho$, respectively. There is general agreement^{3,12} that $(\partial\epsilon/\partial T)_\rho$ is much larger in magnitude, and of opposite sign, than $(\partial\epsilon/\partial T)_\rho$ for typical liquids. In gases at lower densities, the discrepancy between Eqs. (2) and (3) is pronounced, with $(\partial\epsilon/\partial T)_\rho$ being entirely negligible compared with $(\partial\epsilon/\partial T)_\rho$.

In the present paper, we show that the correct form for the energy-balance equations in a single-component transparent fluid is indeed given correctly by Eqs. (1) and (3), in agreement with Refs. 10 and 11. This is important in several ways, which will be discussed more fully in Sec. IV. Among other things, however, (i) the electrocaloric coupling is inconsequential in observations,¹ to date, of STS-I. At the same time electrostrictive effects are as important in giving rise to STS-I as had been supposed for the electrocaloric effect alone^{3,13}; (ii) contrary to existing theory^{1,3,8} there is a vastly reduced influence of the electrocaloric effect on stimulated Brillouin scattering (SBS) and consequently, no possibility for observing an anti-Stokes Brillouin line³ in SBS for transparent fluids.

II. QUALITATIVE CONSIDERATIONS

The results obtained in Sec. III can actually be anticipated from microscopic considerations based on a simple model. Let us envision a box having constant-volume [so that $\partial\rho/\partial t = 0$ in Eq. (1)] low-density ideal-gas atoms, each having small polarizability which remains unaltered during collisions. One asks: Would there be a change in temperature as a uniform electric field is gradually turned on in the space occupied by, and surrounding, the box. Such a change in temperature implies a change in the average kinetic energy of each atom, but there is simply no mechanism for obtaining such a change in energy, since the electric field is uniform, and field-induced acceleration of monatomic atoms can occur only through electric field gradients. Consequently, Eqs. (1) and (3) offer a correct description for this ideal-gas model, since ϵ would depend solely on the density and not at all on temperature,

$$\left(\frac{\partial\epsilon}{\partial T}\right)_\rho = 0,$$

and Eqs. (1) and (3) would predict zero temperature change as E^2 is changed. On the other hand, Eqs. (1) and (2) would lead to a change in temperature as the field is applied, even though microscopically, no mechanism exists for providing the kinetic energy associated with temperature change.

In more realistic situations, translational kinetic

energies can be altered through energy exchange with internal structures which have been influenced by the presence of the uniform field, in analogy with a similar situation in the case of paramagnetic cooling. This effect is also handled appropriately by Eqs. (1) and (3), as will be proven in Sec. III.

III. THEORY

We wish to find the heat input per second per unit volume, (in terms of temperature, density, and electric field) for a dielectric system in the presence of an electric field, assuming time variations to be so slow that thermal equilibrium is maintained throughout. The heat input, related to the entropy S through the expression $T \partial S/\partial t$ is equal, for transparent fluids, to the expression for heating by conduction, $\lambda \nabla^2 T$. To obtain the change in S with electric field, consider the free energy per unit volume F . At constant volume, its differential is given by^{14,15}

$$dF = -S dt + \zeta d\rho + \frac{\vec{E} \cdot d\vec{D}}{4\pi}. \quad (4)$$

The extensive variables in this expression are S , the mass density and \vec{D} , the electric displacement, while the intensive variables are T , the chemical potential parameter ζ , and the electric field \vec{E} . As is well known, the system can be specified by any three of the parameters S , T , ζ , ρ , E , or D . Any four of these parameters can be related through an equation of state. The dielectric constant ϵ , defined (for isotropic media) through the equation $\vec{D} = \epsilon \vec{E}$ can be specified as a function of any three of the variables. For simplicity, however, we view ϵ as a function only of T and ρ , for example, with no dependence on E or D .

Inasmuch as F is a total differential, we wish to express the last term on the right-hand side of Eq. (4) as a total differential together with path-dependent differentials involving $d\rho$ and dT only. To this end, we write

$$\frac{\vec{E} \cdot d\vec{D}}{4\pi} = d\left(\frac{\vec{D}^2}{8\pi\epsilon}\right) + \frac{\vec{E}^2}{8\pi} d\epsilon. \quad (5)$$

By expressing $d\epsilon$ as

$$d\epsilon = \left(\frac{\partial\epsilon}{\partial\rho}\right)_T d\rho + \left(\frac{\partial\epsilon}{\partial T}\right)_\rho dT, \quad (6)$$

the expression for the exact differential $d(F - \vec{D}^2/8\pi\epsilon)$ becomes, with the aid of Eq. (5),

$$d\left(F - \frac{\vec{D}^2}{8\pi\epsilon}\right) = -\left[S - \frac{\vec{E}^2}{8\pi} \left(\frac{\partial\epsilon}{\partial T}\right)_\rho\right] dT + \left[\zeta + \frac{\vec{E}^2}{8\pi} \left(\frac{\partial\epsilon}{\partial\rho}\right)_T\right] d\rho. \quad (7)$$

Following standard procedures,¹⁴ we note that the total differential $d(F - \vec{D}^2/8\pi\epsilon)$ depends only on $d\rho$

and dT . Hence, $d(F - \vec{D}^2/8\pi\epsilon)$ must be equal to its value for zero electric displacement,

$$d\left(F - \frac{\vec{D}^2}{8\pi\epsilon}\right) = dF_0 = -S_0 dT + \xi_0 d\rho, \quad (8)$$

the subscript "0" implying $\vec{D} = 0$. Accordingly,

$$S = S_0 + \frac{\vec{E}^2}{8\pi} \left(\frac{\partial\epsilon}{\partial T}\right)_\rho \quad (9)$$

arises as a direct result of Eqs. (7) and (8). Writing dS_0 in terms of dT and $d\rho$, we find, using well-known Maxwell relations,¹⁵

$$\begin{aligned} TdS_0 &= T\left(\frac{\partial S_0}{\partial T}\right)_\rho dT + T\left(\frac{\partial S_0}{\partial \rho}\right)_T d\rho \\ &= \rho C_v dT - \frac{(\gamma-1)C_v}{\beta} d\rho. \end{aligned} \quad (10)$$

Finally, with the heat input per unit volume given simply through the dissipation term $\lambda\nabla^2 T$, we find

$$\lambda\nabla^2 T = \frac{\partial S}{\partial t} = \rho C_v \frac{\partial T}{\partial t} - \frac{(\gamma-1)C_v}{\beta} \frac{\partial \rho}{\partial t} + \frac{T}{8\pi} \left(\frac{\partial\epsilon}{\partial T}\right)_\rho \frac{\partial E^2}{\partial t} \quad (11)$$

which, upon rearrangement, is simply Eq. (1) with the effective heating term given by Eq. (3).

Similar conclusions may be reached through working with a fixed number of molecules, in which case

$$dF = -SdT - p dv + \frac{\vec{E} \cdot d(\vec{D}v)}{4\pi} - \frac{\epsilon_0 \vec{E}^2}{8\pi} dv \quad (12)$$

represents the free-energy differential associated with changes in T and \vec{D} and the volume v . The last term represents a decrease associated with the fact that field energy is lost from an adjacent external reservoir upon expansion of the system under consideration by an amount dv . The dielectric constant ϵ_0 represents the dielectric constant of the reservoir, differing only by incremental amounts from the dielectric constant ϵ which characterizes the volume v . Since ϵ_0 characterizes an infinite reservoir, it is not sensitive to changes in v , T . By following the same procedures, S is again found as given in Eq. (9), while the pressure is corrected by electrostrictive terms whose (negative) gradient is electrostrictive volume force.¹⁶

IV. DISCUSSION

The most important result stemming from the use of Eqs. (1) and (3) rather than (1) and (2) in nonlinear scattering theory is not that STS-I is now far more difficult to observe than had previously been thought; on the contrary the electrostrictive contribution^{17,18} to STS-I is identical³ with the largest (electrocaloric) contribution arising from the improper use of Eq. (2), the latter being associated with the term $-\beta\rho_0(\partial\epsilon/\partial\rho)_T$ occurring in the expression

$$\left(\frac{\partial\epsilon}{\partial T}\right)_\rho = -\beta\rho_0 \left(\frac{\partial\epsilon}{\partial\rho}\right)_T + \left(\frac{\partial\epsilon}{\partial T}\right)_\rho. \quad (13)$$

Accordingly, for low frequencies ($\omega \lesssim \frac{1}{2}\Gamma_R$, with $\omega_B \gg \Gamma_B, \Gamma_R$), the scattering associated with the proper electrocaloric coupling, Eq. (3) together with electrostrictive effects is the same as that which would result from the improper use of Eq. (2), with electrostrictive effects neglected. In point of fact, however, the scattering at low frequencies (STS-I) is primarily an electrostrictive, rather than electrocaloric effect.

At the same time, Eqs. (1) and (3) do not lead to large electrocaloric-type contributions to the hydrodynamic excitations at higher frequencies ($\omega \approx \omega_B$). Accordingly, SBS phenomena are those which have customarily been considered, without additional contributions associated with the energy-balance equations.^{1,3,8} In particular, the predicted anti-Stokes scattering near critical points is no longer a possibility,¹¹ in accordance with more fundamental considerations.¹⁹

The results of Eqs. (1) and (3) together with the momentum-balance equation containing the electrostrictive coupling can now be summarized by reference to the article by Key and Harrison.³ We would regard the following modifications in their results as being of paramount importance: (a) In Eqs. (17) and (22) of their paper, all electrocaloric terms should be omitted; (b) In Eq. (24) the electrocaloric terms should be omitted where they presently appear in the first group of terms; and one should simply replace (with a minus sign) the second group of electrostrictive terms, which multiplies $(\partial\epsilon/\partial T)_\rho/\beta Y$ in that paper, by the first group. These changes have, in fact, been made by Key and Harrison in their most recent paper.¹¹

*Supported in part by the Office of Naval Research.

¹Present address: Center for Particle Theory, University of Texas, Austin, Tex.

²V. S. Starunov and I. L. Fabelinskii, Usp. Fiz. Nauk **98**, 441 (1969) [Sov. Phys.-Usp. **12**, 463 (1970)].

³I. P. Batra, R. H. Enns, and D. Pohl, Phys. Status Solidi B **48**, 11 (1971).

⁴P. Y. Key and R. G. Harrison, Phys. Rev. A **5**, 1839 (1972).

⁵D. H. Rank, C. W. Cho, N. D. Foltz, and T. A. Wiggins, Phys. Rev. Lett. **19**, 828 (1967).

⁶R. M. Herman and M. A. Gray, Phys. Rev. Lett. **19**, 824 (1967).

⁷G. I. Zaitsev, Yu. I. Kyzylasov, V. S. Starunov, and I. L. Fabelinskii, Zh. Eksp. Teor. Fiz. Pis'ma Red. **6**, 802 (1967) [JETP Lett. **6**, 255 (1967)].

⁸D. I. Mash, V. V. Morozov, V. S. Starunov, and I. L. Fabelinskii, Zh. Eksp. Teor. Fiz. **55**, 2053 (1968) [Sov.

Phys.-JETP **28**, 1085 (1969)].

⁸V. S. Starunov, Zh. Eksp. Teor. Fiz. **57**, 1012 (1969) [Sov. Phys.-JETP **30**, 553 (1970)].

⁹W. H. Lowdermilk and N. Bloembergen, Phys. Rev. A **5**, 1423 (1972).

¹⁰N. M. Kroll and P. L. Kelley, Phys. Rev. A **4**, 763 (1971).

¹¹P. Y. Key and R. G. Harrison, Phys. Rev. A **6**, 1258 (1972); R. G. Harrison, P. Y. Key, and V. I. Little, Proc. R. Soc. Lond. (to be published).

¹²I. P. Batra and R. H. Enns, Phys. Rev. **185**, 396 (1969).

¹³Inasmuch as the spatial gain in STS-I is comparable, in typical liquids, with that associated with STS-II for very small extinction coefficients (5×10^{-4} for benzene) lying well below the critical value predicted for realistic experiments (Refs. 2, 4, and 5), it is difficult to explain the observations of an unshifted line in conventionally clear liquids as being due to either cause. A

possible alternative explanation might be that the heat deposited through vibrational relaxation following stimulated Raman scattering (SRS) gives rise to an effective STS.

¹⁴L. D. Landau and E. M. Lifshitz, *Electrodynamics of Continuous Media* (Pergamon, London, 1960).

¹⁵H. B. Callen, *Thermodynamics* (Wiley, New York, 1960).

¹⁶W. K. H. Panofsky and M. Phillips, *Classical Electricity and Magnetism* (Addison-Wesley, Reading, Mass., 1962).

¹⁷M. A. Gray, Ph.D. thesis (The Pennsylvania State University, 1968) (unpublished).

¹⁸W. Rother, Z. Naturforsch. **25A**, 1120 (1970).

¹⁹Anti-Stokes two-photon scattering, without accompanying optical absorption, implies a lowering of total energy of the low-temperature scattering medium accompanying the increase in optical energy, with no further side effects—in violation of the second law of thermodynamics.

PHYSICAL REVIEW A

VOLUME 7, NUMBER 4

APRIL 1973

Low-Energy-Electron Scattering Amplitudes. II. Validity of Free-Electron-Gas Exchange Approximations Applied to Electrons Incident on Hg

D. Gregory* and M. Fink*

Physics Department and Electronic Research Center, The University of Texas at Austin, Austin, Texas 78712

(Received 6 July 1971)

For the test case of 300-eV electrons incident on Hg the influence of the exchange of the incoming electron with the atomic electrons is studied. Four different approximations for the derivation of an exchange potential based on the free-electron-gas description are discussed. These approximate exchange potentials were employed in calculations of electron scattering factors. The comparison of those results with a rigorous Hartree-Fock (HF) treatment of the total scattering problem ($N+1$ particles) shows that the exchange given by Kohn and Sham is too large, especially at large atomic distances. By Gombás's introduction of a cutoff at the radius of the Thomas-Fermi-Dirac atom, the long tail of the potential was avoided. While the truncated results of Gombás decrease the deviations significantly, a different treatment of the self-exchange as suggested by Lindgren and Rosen brings the best agreement with the HF calculation. The theoretical results show that precise relative measurements in the valleys of the different cross sections are an extremely sensitive tool for testing scattering theory.

I. INTRODUCTION

At present there are two rather different approaches employed in calculating elastic differential cross sections for moderate-energy electrons (300 eV) incident on gaseous systems. The extended polarization potential approximation of LaBahn and Callaway treats the scattering problem by Hartree-Fock (HF) perturbation theory.¹ This approach takes into account adiabatic (energy-independent) charge cloud polarization effects and exchange of atomic electrons with each other as well as with the incoming electrons. However, correlation effects have to be neglected, and the method is too complicated to be extended to heavy atoms like Hg.

The second technique used to calculate scattered intensities is based on the static-potential theory. This approach utilizes the best available wave functions of the unperturbed target to calculate

cross sections, spin polarization, and other effects.² It can be applied to any atom. However, the changes of the differential cross sections due to such effects as the exchange of the incoming electrons and the charge cloud polarization have to be calculated by finding correction terms to the static atomic potential. With this corrected potential, new scattering factors are calculated which include the effects in an approximate way. It is our purpose to compare the various approximate corrections to the static potential that have been proposed to account for exchange scattering. We will then discuss the effects of these exchange potentials on the corresponding theoretical elastic differential cross sections.

The exchange of all electrons can be included rigorously for electrons scattered from an N -electron atom by numerically solving the $N+1$ many-body problem with a HF treatment, as was done by Walker for Hg.³ With respect to the effect of