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FIRST SOUND AND QUANTUM EFFECTS IN LIQUID NEON

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Résumé. — Récemment des expériences acoustiques ont confirmé la possibilité que, dans le néon liquide, la vitesse du son présente une dispersion négative — faible mais significative — conformément aux prédictions faites à partir d'expériences de diffusion Brillouin. Les mesures considérées tant acoustiques qu'optiques, ont été effectuées le long de la courbe de tension de vapeur, depuis le point triple jusqu'au-delà du point d'ébullition normale, où une anomalie avait été remarquée pour la conductibilité thermique ainsi que pour la viscosité tangentielle. Il n'y a, par contre, en ce qui concerne la chaleur spécifique, aucune indication d'un comportement particulier dans ce domaine de température. Semblablement, ni la vitesse ultrasonique ni la vitesse hypersonique ne semblent manifester d'anomalie évidente autour du point d'ébullition normale. Par contre la comparaison entre les résultats ultrasoniques (à 30 MHz et à 1,3 MHz) et les valeurs correspondantes obtenues à partir des expériences de diffusion Brillouin indique que la vitesse hypersonique (à 2 GHz) est toujours de 1/2 à 1 1/2 % plus faible que la vitesse mesurée à basse fréquence. Une comparaison semblable dans le cas de l'Argon liquide paraît également indiquer l'existence d'une dispersion négative en accord qualitatif avec les prédictions théoriques, basées sur la forme généralisée des coefficients de transport à fréquence finie et obtenues à partir du spectre des fluctuations de densité calculé au second ordre. Toutefois de tels effets ne peuvent induire qu'une dispersion nettement plus faible que celle observée dans le néon liquide. Ici, le caractère partiellement quantique du Néon pourrait s'avérer responsable de la déviation observée. Cette suggestion est basée sur une évaluation effectuée à partir du théorème des états correspondants. On obtient un accord semi-quantitatif entre l'estimation théorique et la dispersion observée.

Abstract. — Recent ultrasonic measurements have confirmed the possible existence of a small but significant negative dispersion in the sound velocity in liquid neon as predicted from Brillouin scattering experiments. The acoustic and the optical experiments were performed along the saturated vapor pressure curve from the triple point to above the normal boiling point, where an anomaly had been reported for the thermal conductivity and for the shear viscosity, whereas there was no indication of any particular behavior in the specific heat. Neither does the ultrasonic velocity nor the hypersonic velocity exhibit evidence for the existence of an anomaly around the normal boiling point. On the other hand comparison of the ultrasonic data (at 30 MHz and 1.3 MHz) with the corresponding values as obtained from Brillouin scattering experiments indicates that the hypersonic velocity (~ 2 GHz) is always lower than the low frequency velocity by 1/2 to 1 1/2 %, a discrepancy which exceeds the experimental errors. A similar comparison in the case of liquid argon seems to indicate the existence of a negative dispersion in the sound velocity in agreement with theoretical predictions, based on the frequency dependence of the transport coefficients and on second order effects in the spectrum of the density fluctuations. However such effects are much smaller than the dispersion measured in liquid neon where quantum effects might be responsible for the observed deviation. This behavior is in semi-quantitative agreement with the evaluation based on the Principle of Corresponding states.

I. Introduction. — In the study of hydrodynamics and of thermodynamics of simple liquids Neon occupies a peculiar and interesting position, intermediate between the classical monatomic liquids (Ar, Kr, Xe) and Helium. For instance if one considers the classical limit to be satisfied when the average distance moved is large compared to the characteristic atomic wavelength, then for a classical fluid

$$\kappa > k^{(1)}, \quad (1.1)$$

where κ is the characteristic wavenumber defined by

$$\kappa = \frac{(2 m \varepsilon)^{1/2}}{\hbar}, \quad (1.2)$$

with m , the mass ; ε , the minimum of the intermolecular potential curve ; and $\hbar$, Planck's constant. Here $k^{(1)}$ is the position of the first peak of the structure factor, $S(k, \omega)$. Condition (1.1) is satisfied for Argon (whereas the inequality is reversed for Helium) and is not satisfied for Neon [1].

The fact that Neon exhibits a non negligible quantum character has been seen to play a significant role in thermodynamic equilibrium properties [2]. What the influence of this quantum character would be on non equilibrium properties is much less well known, both from the experimental and theoretical viewpoints. For instance in the last decade experimental data have suggested the existence of anomalies in the shear viscosity [3] and in the thermal conductivity [4] of liquid Neon around the normal boiling point (NBP),

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whereas there is no indication of any particular behavior in the specific heat [5]. It has also been observed that Neon does not always follow the Principle of Corresponding States as the other simple molecules do. For instance, to fit the reduced shear viscosity of liquid Neon to the universal function, $\eta^*(T^*)$, where T^* is the reduced temperature, a temperature adjustment is necessary [6], suggesting in this way the existence of a « degeneracy temperature » for Neon.

Comparison of recent first sound measurements in liquid Neon indicates that the hypersonic velocity [7], v_s , is always smaller than the ultrasonic velocity [8], u_s . Namely one observes experimentally an average negative dispersion of $\sim 1.2\%$, as shown in table 1.

TABLE I
Sound velocity in saturated liquid neon

T (°K)	v_s (m/s) (*)	u_s (m/s) (**)	$(u_s - v_s)/u_s$ (%)
25	619.3	628.3	1.4
26	601.0	612.5	1.9
27	588.4	596.4	1.3
28	574.0	579.6	1.0
29	558.0	562.3	0.8
30	540.0	544.5	0.8

(*) Hypersonic velocity (at 1.5-2.0 GHz) from Fleury and Boon [Ref. 7].

(**) Ultrasonic velocity (at 1.2-1.4 MHz) from Güsewell, Schmeisser, and Schmid [Ref. 8].

While ultrasonic frequencies belong strictly to the domain of classical hydrodynamics (characterized by the limits, $k \rightarrow 0$, $\omega \rightarrow 0$), the frequency shift measured in Brillouin scattering ($\omega/\omega_c \sim 10^{-2}$, where ω_c^{-1} is of the order of the collision time) places the domain of light scattering in a region intermediate between classical hydrodynamics and generalized hydrodynamics (characterized by $\omega/\omega_c \sim 1$ and $k/k_c \sim 1$, where k_c^{-1} is of the order of the intermolecular distance). In Section 2 we briefly recall the consequences this difference between ultrasonics and Brillouin scattering might have on the first sound velocity, and in particular how such a difference could be responsible for the existence of a negative dispersion. In the case of liquid Argon, such effects would indeed induce a small dispersion [9] in qualitative agreement with the experimental observation [7], [10]. In a classical fluid, like liquid Argon, such effects are extremely small and barely detectable, whereas in liquid Neon the observed dispersion exceeds the experimental errors and appears to be much larger than the effects which arise from higher order corrections in the intermediate domain defined above. In Section 3, we examine the effect of the partial quantum nature of Neon on the sound velocity. Because of the lack of a rigorous quantum theory of sound propagation, we

turn to a phenomenological approach based on the Theorem of Corresponding States. We find a quantum correction to the « classical » sound velocity which amounts to $\sim -2\%$, whereas second order effects at high frequencies in the intermediate domain contribute only $10^{-2} - 10^{-3}\%$.

In view of the fact that the estimated quantum correction to the sound velocity yields a value which corresponds semi-quantitatively to the observed dispersion, one is led to the following questions: If the observed dispersion is not an artefact, is the « agreement » a coincidence? If not, then, what is the connection between dispersion effects and quantum effects?

The present paper has as its primary purpose to investigate these questions phenomenologically and to provide motivation for further experiments in both Ne and other quantum liquids (H_2 , D_2 and He^I).

2. Dispersion effects. — Consider the dispersion curve as obtained from the structure factor, $S(k, \omega)$; one observes [1], [11] that the (ω, k) plane may be separated roughly into two regions: the *hydrodynamic domain*, characteristic of collective modes, and defined by

$$\lim \omega = 0, \quad \lim k = 0, \quad (2.1)$$

and the domain of *generalized hydrodynamics*, the kinetic region, for which

$$\frac{\omega}{\omega_c} \sim 1, \quad \frac{k}{k_c} \sim 1, \quad (2.2)$$

where ω_c and k_c are defined in Section 1.

Now in light scattering experiments, k is typically of the order of 10^5 cm^{-1} , i. e. $k/k_c \sim 10^{-3}$, whereas Brillouin shifts are measured in the GHz region, i. e. for a simple monatomic liquid ω/ω_c becomes of the order of 10^{-2} . Such a value is still far from the ratio characteristic of the generalized hydrodynamic domain, implying that the classical hydrodynamic approach is still basically valid, provided one accounts for the existence of a not strictly zero value of ω . It is then expected that in this *intermediate region*, where ω/ω_c is finite but small, some new effects might be observed as small deviations from classical hydrodynamics. This intermediate domain has been studied recently by Boon and Deguent [8] (BD). The basic idea of the BD treatment arises from the observation that at finite frequency the transport coefficients become ω -dependent. Therefore the usual coefficients in the hydrodynamic equations should be replaced by *transport functions*, leading to a new dispersion equation where from the hydrodynamic modes are calculated. We shall concentrate here on the BD result for the frequency of the thermal phonons in the intermediate region. The Brillouin shift reads

$$\omega_B = \pm c_0 k(1 - \delta^{(2)} - \delta^{(\omega)}), \quad (2.3)$$

with c_0 the zero frequency sound velocity ($c_c \equiv u_s$). Here $\delta^{(2)}$ is a pure second order correction in $\Gamma k/c_0$, where Γ is the appropriate linear function of the transport coefficients appearing as a combination of the classical expressions for the linewidths of the Brillouin and the Rayleigh peaks [12]. $\delta^{(\omega)}$ denotes the term containing the high frequency effects, i. e. the non-dissipative part of the transport functions, and appears also as a second order correction in $\Gamma k/c_0$. These different contributions were evaluated for liquid Argon. Most important is the observation that $\delta^{(\omega)}$ is negative, inducing therefore a *positive dispersion* whereas $\delta^{(2)}$ being positive and larger than $\delta^{(\omega)}$ yields a total *negative dispersion*. This evaluation is in qualitative agreement with the experimental observation by Fleury and Boon [7]. It is interesting to notice that the *actual* dispersion effect, i. e., the effect arising from the term $\delta^{(\omega)} = f(\omega/\omega_c)$ is positive although the total effect, namely

$$\delta^{(\omega)} < 0, \text{ and } \delta^{(2)} > 0, \text{ with } |\delta^{(2)}| > |\delta^{(\omega)}|,$$

$$|\omega_B| < c_0 k, \text{ or } \frac{v_s - c_0}{c_0} < 0, \quad (2.4)$$

appears to be indebted to the relaxation effects. This is also in agreement with Chung and Yip generalized hydrodynamic theory [13].

Despite the lack of numerical data which precludes accurate evaluations for the case of liquid Neon, one

expects $\delta^{(2)}$ and $\delta^{(\omega)}$ to be of the same order of magnitude for all simple monatomic liquids. Since those corrections are not larger than 10^{-4} , they cannot account for the dispersion observed in liquid Neon. Indeed comparison of the ultrasonic data [8] with the light scattering data [7] yields

$$\frac{u_s - v_s}{u_s} \Big|_{\text{exp}} \simeq 1.9 - 0.5 \%, \quad (2.5)$$

(experimental extreme values for $25^\circ\text{K} \leq T \leq 30^\circ\text{K}$) as shown in figure 1 [14]. It is also important to notice that this difference exceeds the experimental errors. This point will be discussed in Section 4. Although a slight slope change in the temperature dependence of the hypersonic velocity was initially mentioned by Fleury and Boon [8], when their pressure readings are converted into temperature according to Grilly [14], there is no real evidence for such a slope change.

3. Quantum effects. — As mentioned in Section 1, Neon might appear as a good candidate for the investigation of « anomalous » high frequency behavior because it can be considered as a semi-quantum fluid. Here « anomalous behavior » should be understood in the sense of exhibiting deviations from classical hydrodynamics in the *intermediate region*, defined above. The partial quantum nature of Neon can also be seen by considering the reduced de Broglie wavelength, or the de Boer parameter, defined by [2]

$$\Lambda^{*2} = \frac{\hbar^2}{m\sigma^2\varepsilon}, \quad (3.1)$$

where σ and ε are the characteristic parameters of the intermolecular potential curve.

If one sets $\Lambda^* = 1$ for helium, and $\Lambda^* = 0$ for xenon, then [15], $\Lambda^* (\text{neon}) = 0.13$. Now why and how quantum effects would play an important role in high frequency phenomena remains an open question. In view of the lack of any theoretical treatment of this problem, we shall turn to a phenomenological approach based on the Principle of Corresponding States [2]: our purpose is to evaluate the order of magnitude of the quantum effect to the sound velocity. Along the saturated vapor-pressure curve of a classical fluid, the reduced velocity may be written as a universal function of the reduced temperature, i. e.

$$v^*(T^*) = \chi^{-1} v(T), \quad (3.2)$$

with

$$\chi = \left(\frac{\varepsilon}{m}\right)^{1/2}, \quad (3.3)$$

and

$$T^* = \frac{kT}{\varepsilon}. \quad (3.4)$$

FIG. 1. — The sound velocity in liquid Neon versus temperature, along the saturated vapor pressure curve, as obtained from ultrasonic measurements (●, ▲; reference [8]) and from light scattering experiments (□; reference [7]). Also shown are the classical, v^{CL} , and quantum, v^Q , evaluations from the principle of Corresponding States.

Eq. (3.2) holds for those substances which obey the law of Corresponding States (namely spherically symmetric molecules without internal degrees of freedom and whose intermolecular potential can be cast in the form of a universal function, $\varepsilon(r) = \varepsilon\Phi(r/\sigma)$), and is indeed well satisfied for Argon, Krypton and Xenon [16]. Now for quantum systems, the reduced sound velocity is also a function of Λ^{*2} , which follows from the fact that the expansion of the scattering cross-section for small and moderate wavelengths is even in $\hbar$. For instance, one observes [17] that the reduced sound velocity for substances like Helium (and Hydrogen) does not coincide with the universal function, $v^*(T^*)$, of the classical molecules (Ar, Kr, Xe) with $\Lambda^* \simeq 0$. For a substance whose quantum parameter Λ_j^* is finite but not too large, we may perform an expansion to obtain (at the same reduced temperature T^*)

$$v^*(\Lambda_j^{*2}) = v_{\text{CL}}^*(\Lambda_i^* \simeq 0) \left[1 + \Delta\Lambda^{*2} \frac{\partial \ln v^*}{\partial \Lambda^{*2}} \bigg|_{\Lambda_i^*} \right], \quad (3.5)$$

with

$$\Delta\Lambda^{*2} = \Lambda_j^{*2} - \Lambda_i^{*2}. \quad (3.6)$$

Here v_{CL}^* is the corresponding classical value of v^* , i. e. the reference species (labeled with subscript i) is e. g. Argon which has a very weak (and quite negligible) quantum character. Indeed, one has [15]

$$\Lambda_{\text{He}}^{*2} = 9.43; \quad \Lambda_{\text{Ne}}^{*2} = .352; \quad \Lambda_{\text{Ar}}^{*2} = .035. \quad (3.7)$$

Now, the analytic form of the function $v^*(\Lambda^{*2})$ is not known explicitly, but in order to calculate the RHS of eq. (3.5), we may obtain an evaluation of the slope $\partial \ln v^* / \partial \Lambda^{*2}$ from a graphical representation of the data available for simple fluids as shown in figure 2.

FIG. 2. — The reduced sound velocity as a function of the de Boer parameter (from references 7, 8, 10, 16 and 17).

One then obtains simply from eqs. (3.2)-(3.6) the sound velocity

$$v_j(T) = v_i(T_{\text{corr}}) \left(\frac{\varepsilon_j m_i}{\varepsilon_i m_j} \right)^{1/2} \frac{v^*(\Lambda_j^{*2})}{v^*(\Lambda_i^{*2})}, \quad (3.8)$$

where the sound velocity of the reference substance is to be taken at a corrected temperature : $T_{\text{corr}} = T\varepsilon_i/\varepsilon_j$. The corresponding value for the classical sound velocity is simply obtained from eq. (3.2) (or from eq. (3.8) where omitting the last factor on the RHS).

For liquid Neon, we obtain from eq. (3.2) and (3.8)

$$\frac{v^{\text{CL}} - v^{\text{Q}}}{v^{\text{CL}}} \bigg|_{\text{calc}} \sim 2 \%. \quad (3.9)$$

The calculated absolute values of the classical sound velocity, v^{CL} , and of the quantum corrected sound velocity, v^{Q} , are plotted in figure 1 along with the experimental data. Although the slopes of the experimental data do not coincide with those of the calculated values, one observes that v^{CL} corresponds roughly to u_s , the ultrasonic velocity data, whereas v^{Q} reproduces quite reasonably the hypersonic data, v_s . The rather poor agreement between the calculated values and the experimental data is not surprising, since it is not expected that the principle of Corresponding States be a good method for the evaluation of absolute quantities; however the method is quite well appropriate for the calculation of relative values. Therefore most important is the observation that the classical and quantum estimates ratio, eq. (3.9), corresponds rather closely to the observed dispersion, eq. (2.5).

4. Discussion. — In view of the results presented in the previous sections, we are led to a series of questions, the first one being : could the discrepancy between u_s and v_s be due to experimental errors ? We already mentioned that the observed dispersion exceeds the experimental errors. The ultrasonic data arise from two different sources [8] and are in excellent agreement, i. e. the values from the two different sources lie within $\pm 0.1 \%$ of each other, well within the experimental accuracy of either data set, $\pm 0.2 \%$ and $\pm 0.3 \%$, respectively. In the Brillouin scattering experiments [7], the different experimental errors may arise from : the measurement of the scattering angle ($\pm 0.1 \%$); the evaluation of the refractive index ($\pm 0.01 \%$); the Fabry-Perot spacer ($\lesssim \pm 0.1 \%$); the Rayleigh pulling ($\lesssim \pm 0.2 \%$); the chart measurements ($\pm 0.3 \%$); and the temperature (or pressure) readings ($\pm 0.03 \%$). Even if all the errors would add up systematically (which is very unlikely) the total error should not exceed 0.7% .

Now, could there be a systematic temperature shift ? Indeed, the two sets of data, u_s and v_s (Fig. 1) lie quite parallel to each other so that a shift of $\sim 0.35 \text{ }^\circ\text{K}$ would make them coincide. However this would mean an error $> 100 \text{ mm Hg}$ in the pressure readings, which is far beyond the experimental uncertainty ($\pm 3 \text{ mm}$

corresponding to $\pm .01$ °K). Notice that when considering the « degeneracy temperature » [2]

$$T_D = \frac{\hbar^2}{m\sigma^2 k} = \frac{\Lambda^{*2} \varepsilon}{k}, \quad (3.10)$$

for Neon (with $\varepsilon/k = 36$ °K), one finds

$$T_D(\text{Neon}) \cong 0.35 \text{ °K}. \quad (3.11)$$

The « degeneracy temperature » defines an effective temperature, $T_{\text{eff}} = T - T_D$, towards which the classical quantity considered is shifted because of the quantum effects (when $\Lambda^* = 0$, $T_D = 0$). The value obtained here (3.11) corresponds quite well to the temperature shift necessary to make u_s and v_s coincide. Now if the discrepancy between u_s and v_s is real, this observation would indicate the possible existence of a negative dispersion in the first sound of liquid Neon. This then leads us to the following speculation : unless the experimental dispersion appears to be an artefact,

is it merely a coincidence that quantum effects account semi-quantitatively for the observed negative dispersion ? If not, then we are led to the following unanswered question : why should quantum effect be frequency dependent ? Indeed, in the case of liquid Argon [7], one observes a very small effect, if any. For liquid Neon, the experimental observation indicates the possible existence of a larger dispersion. Then, if there is any correlation between quantum effects and dispersion effects, the phenomenon should also be observed in the normal fluid region of ^4He . Very recent measurements [18] however seem to indicate that, if dispersion occurs indeed in liquid ^4He , the effect is probably not larger than 0.5 %.

No unambiguous conclusion could be drawn before further experimental evidence of the phenomenon. The most convincing test will be provided by very accurate and simultaneous measurements of the ultrasonic and hypersonic velocities under rigorously the same experimental conditions.

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