

Effects of pressure on electronic bubbles in liquid neon†

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Abstract. A calculation is performed for the ground state energy of an electronic bubble in liquid neon as a function of temperature and pressure, and using experimentally determined electron–neon scattering cross sections. The density of the compressed liquid is calculated from an equation of corresponding states. It is found that the electronic bubble should collapse at temperatures near T_c with a few atmospheres of overpressure.

1. Introduction

Recent measurements of the mobility of electrons injected in liquid neon suggest the existence of localized electron states (Bruschi *et al* 1972, Loveland *et al* 1972), the nature of these states probably being the same as that invoked to explain analogous measurements in liquid He (Jortner *et al* 1965, Springett *et al* 1967, 1968, Miyakawa *et al* 1969). These authors proved that the ground state of an excess electron in liquid He is a bubble with the electron confined in it. In this system the electron localization is due to the electron–helium atom repulsion (Pauli principle) which is large with respect to the polarization potential of He, as shown by the positive scattering length λ of low energy electrons against He-atoms ($\lambda = 1.2a_0$, with a_0 the Bohr radius: O'Malley 1963).

On the basis of the positive sign of the scattering length, liquid neon was the only other rare-gas liquid which might be considered as a candidate for the formation of stable localized electron states. Indeed, Springett *et al* (1968) and Miyakawa *et al* (1969) showed in their calculations that bubble states could be stable in liquid Ne, but the small values of λ and the large uncertainty in its experimental determination did not allow a definite prediction. In addition, while Springett *et al* (1968) found that in He a bubble collapse could occur at pressures higher than the melting pressure, and then it would never be observable in the liquid, in Ne the behaviour of bubbles under pressure was never studied.

In view of a systematic experimental investigation, it is interesting to study this behaviour even with a simple, semiclassical model. Our aim is then to see if it is possible to reach the critical pressure for bubble collapse in the liquid and to give an estimate of such a pressure. In this work we will use the model of Springett *et al* (1967) and Miyakawa *et al* (1969) to study the stability of the bubble under pressure in liquid neon. It must be emphasized that while this model has given results in agreement with experiments for

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liquids, its application to experiments in gases is less satisfactory. Even if it can in principle be used to study excess electrons in gases, its failure to explain the mobilities observed in He-gas by Levine and Sanders (1967) suggests the use of a more refined, entirely quantum mechanical model in this situation.

2. The model

We consider a very simple model for the electron–bubble complex in liquid neon. When we have a localized electron, the liquid exhibits an abrupt change in its number density n , n being zero in a spherical cavity around the electron and equal to the mean number density n_0 outside it. Electrostriction effects which cause the density to increase around the cavity are thus neglected. The electron is thought to be in a spherical square well potential whose depth is $-(E_0 + E_K)$ with respect to the liquid. Here E_0 is the potential barrier seen by an electron injected into the liquid, ie the energy of a quasi-free electron in the liquid with respect to vacuum. E_K is the change in field energy due to the fact that the electron is no longer surrounded by a uniform liquid but is in an empty cavity. In addition to the potential energy, the electron, in its ground state, will have the energy E_e corresponding to the lowest state (ie 1s state) in the square well of radius R . In order to calculate the total energy of the electron–bubble complex we must add to the electron energy the energy spent to create the bubble, consisting of a surface energy E_s and of a volume energy $E_v = \frac{4}{3}\pi R^3 p$, this last term corresponding to the work done against pressure to form the cavity. Therefore, the total energy of the complex will be

$$E = -E_0 - E_K + E_e + E_s + E_v, \quad (1)$$

and the condition for bubble stability is $E < 0$; if $E > 0$ the electron in the liquid is quasi-free. We shall now discuss how to evaluate the terms E_0 , E_K , E_s in equation (1). E_0 is calculated using the Wigner–Seitz approximation, namely the liquid is considered as a uniform distribution of hard core molecules with radius equal to the scattering length λ , each one of them at the centre of a sphere with radius

$$r_s = \left(\frac{3}{4\pi n_0} \right)^{1/3}. \quad (2)$$

The continuity of the electron wavefunctions, together with their derivatives, at the surface of the Wigner spheres gives the following eigenvalue equation for k_0 , the lowest electron wavenumber:

$$\operatorname{tg} k_0 (r_s - \lambda) = k_0 r_s. \quad (3)$$

We note that the experimental values of λ in neon range from $0.24a_0$ to $0.39a_0$ (a_0 = Bohr radius), and that Thompson (1966) obtained the value $\lambda = 0.347a_0$ from a phase shift calculation for scattering of an electron by atomic neon. In the framework of the model described here, at vapour pressure, Miyakawa *et al* (1969) showed that the bubble should be stable at any temperature if $\lambda = 0.39a_0$, while it would always be unstable if $\lambda = 0.24a_0$. In the light of the experimental results (Bruschi *et al* 1972 Loveland *et al* 1972) it seems then appropriate to use values of λ near $0.39a_0$. We report here results of calculations for two values of λ , namely $\lambda = 0.39a_0$ and the theoretical value $\lambda = 0.347a_0$. In figure 1, E_0 is shown as a function of n_0 for these two values.

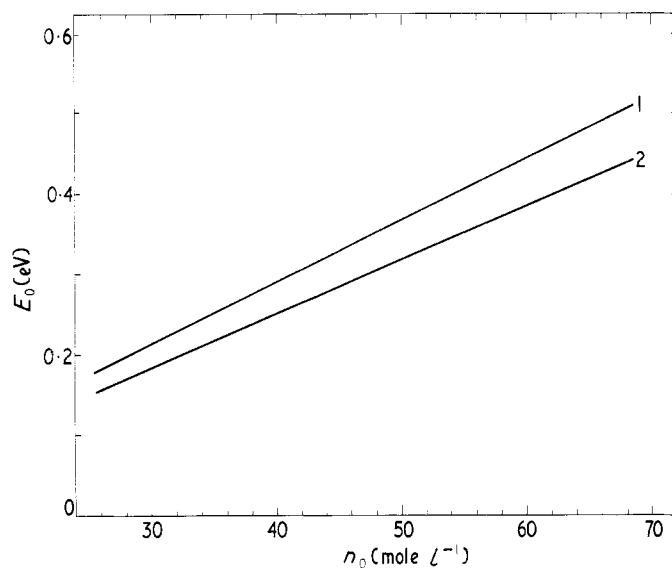


Figure 1. E_0 plotted against density. Curve 1: $\lambda = 0.390a_0$. Curve 2: $\lambda = 0.347a_0$.

E_K is easily calculated by means of elementary electrostatic theories in dielectrics, yielding:

$$E_K = \frac{K-1}{K} \frac{e^2}{2R} \quad (4)$$

where K is the dielectric constant of neon.

The last term to be considered is E_s : Miyakawa *et al* (1969) used

$$E_s = 4\pi R^2 \sigma \quad (5)$$

where σ was taken as the macroscopic surface tension at vapour pressure, related to the temperature by the relationship:

$$\sigma = \gamma_0 \left(1 - \frac{T}{T_c}\right)^b \quad (6)$$

with $\gamma_0 = 15.20 \text{ erg cm}^{-2}$, $T_c = 44.38 \text{ K}$ and $b = 1.216$ for neon.

One must however be very cautious in using this expression in compressed liquids, first of all because we are dealing with a microscopic surface and secondly because we are studying a very peculiar bubble which is not sustained by the pressure of a vapour inside it.

If this were the case, we could simply relate σ to the liquid density outside the bubble and the vapour density inside it using the parachor equation.

In our case the cavity can be considered empty, and one should calculate the work done to expand such a cavity in the liquid. Reiss *et al* (1960) showed that this work can be expressed as a function of the bubble radius by the relationship:

$$W(R) = 4\pi\sigma_0 \left(1 - \frac{2\delta}{R}\right) R^2 + E_v, \quad (7)$$

with

$$\sigma_0 = \frac{kT}{4\pi a^2} (x + 18x^2) - \frac{1}{2}pa, \quad (8)$$

$$\delta = \frac{a}{4} \left| \frac{6x + 18x^2 - \pi pa^3/kT}{6x + 9x^2 - pa^3/kT} \right|, \quad (9)$$

$$x = \frac{\pi n_0 a^3/6}{1 - \pi n_0 a^3/6}, \quad (10)$$

where a is the radius at which the neon-neon Lennard-Jones potential is zero, T the temperature, p the pressure of the liquid, n_0 its density and k the Boltzmann constant.

We have therefore evaluated the various terms of equation (1); to find the most stable configuration we will minimize E with respect to R . If $E_{\min} < 0$, the electron ground state in the liquid will then be an electronic bubble of radius R_{\min} . On the other hand for $E_{\min} > 0$ the bubble model loses validity and the ground state will be the quasi-free electron state with energy E_0 .

We remark at this point that all the terms appearing in equation (1) depend on the liquid density; since our aim is to study the behaviour of an extra-electron in compressed liquid neon, we must then determine the density of such a liquid. To our knowledge, only two papers report measurements of the density of compressed liquid neon. Lippold (1969) has reported measurements obtained by a difference method for pressures ranging from 10 kg cm^{-2} to 1000 kg cm^{-2} along 7 isotherms between 28.37 K and 43.11 K. Gibbons (1969) gave 309 points on the PVT surface of neon between 27 K and 70 K. Unfortunately the two sets of data are not satisfactory for our purposes: in fact Lippold's data were taken at too high pressures and would not allow a systematic study of E for pressures between vapour pressure and 100 kg cm^{-2} , while Gibbons' points are scattered on the PVT surface, thus making it impossible to follow the behaviour of E along low isotherms or isobars. For these reasons we calculated the density from an equation of corresponding states obtained by Holleran (1971) which reproduced accurately the experimental data for various compressed liquids. Such an equation expresses the compressibility factor of a liquid, $Z = P/n_0RT$ (R is the perfect gas constant), in terms of a reduced temperature $\theta = T/T_B$, a reduced density $\eta = n_0/n_B$ and a non-ideality constant K_B , with T_B and n_B constants.

$$Z = 1 + K_B \eta \left(\frac{1}{1 - \eta} - \frac{1}{\theta} \right) \left(\frac{1 - \eta}{\theta} \right)^{1.75 \eta^{-1}}. \quad (11)$$

For neon the three constants assume the values

$$T_B = 134 \text{ K} \quad n_B = 79 \text{ mole/litre} \quad K_B = 1.42.$$

Equation (11) was solved on a computer and the densities so obtained for $p = p_v$ were checked against the corresponding experimental data (Johnson 1960). The accuracy with which the experimental results were reproduced was found to be a decreasing function of temperature so that we used equation (11) only up to $T = 37.61 \text{ K}$ where the error is 2.2%. A check was made also against Lippold's data to look at the pressure dependence of the error made on n_0 . We found that at high pressures the solutions of equation (11) reproduce the experimental results within 0.4% in the entire temperature range, as previously found by Holleran. In table 1 we report the densities calculated from equation (11) along 6 isotherms at various pressures.

Table 1. Densities of compressed liquid neon as calculated from equation (11). Values in parenthesis are the experimental data at vapour pressure (Johnson 1960)

$T = 25.6 \text{ K}$		$T = 26.43 \text{ K}$		$T = 29.69 \text{ K}$	
$p \text{ atm}$	$n_0 \text{ mole/l}$	$p \text{ atm}$	$n_0 \text{ mole/l}$	$p \text{ atm}$	$n_0 \text{ mole/l}$
0.594	60.94 (60.99)	0.796	60.20 (60.46)	2	57.06 (57.48)
10.594	61.21	10.796	60.49	10	57.39
20.594	61.47	20.796	60.77	20	57.78
30.594	61.72	30.976	61.04	30	58.15
38.594	61.92	38.796	61.25	38	58.43
60	62.41	60	61.77	60	59.15
		72	62.05	72	59.51
		96	62.58	96	60.17

$T = 32.69 \text{ K}$		$T = 34.70 \text{ K}$		$T = 36.2 \text{ K}$	
$p \text{ atm}$	$n_0 \text{ mole/l}$	$p \text{ atm}$	$n_0 \text{ mole/l}$	$p \text{ atm}$	$n_0 \text{ mole/l}$
4	53.82 (54.26)	6	51.36 (51.93)	8	49.20 (50.30)
10	54.18	10	51.69	10	49.42
20	54.74	20	52.43	20	50.41
30	55.25	30	53.09	30	51.25
38	55.63	38	53.57	38	51.84
60	56.56				
72	57.02				
96	57.86				

The energy E was then calculated using the densities obtained from equation (11) for $T_i < T \leq 37.61 \text{ K}$ with pressures ranging from p_v up to 100 atm. For higher pressures and higher temperatures we used Lippold's data, while for $T > 37.61 \text{ K}$ and $p < 100 \text{ atm}$ Gibbons' points were adopted.

3. Results and conclusions

In figure 2, where the energy E at vapour pressure is plotted against temperature for the two values of λ considered here, one notices a striking difference between Miyakawa's *et al* (1969) results and ours. In our treatment based on equation (7) for the surface tension, the energy E increases with temperature, while Miyakawa's curve for the same quantity, obtained using equation (6) for σ , displays a minimum at $T \simeq 40 \text{ K}$. In addition one sees from figure 2 that if $\lambda = 0.347a_0$, the bubble becomes unstable at low temperatures if $\sigma = \gamma_0 (1 - T/T_0)^b$ while the instability occurs at high temperatures if $\sigma = \sigma_0 (1 - 2\delta/R)$. This effect can be explained by observing the different behaviour of the expression for the surface energy; while at low temperature the first is large and then acts to delocalize the electron, it becomes negligibly small at higher temperatures (near T_0), where the second still gives an important positive contribution to the total energy E .

We believe that only the expression $\sigma = \sigma_0 (1 - 2\delta/R)$ is meaningful for the 'empty' bubble, and thus we will only comment on the results obtained by using it. Increasing pressure (figure 3) causes the binding energy at a given temperature to diminish, thus lowering the temperature at which the instability should occur. We point out that at

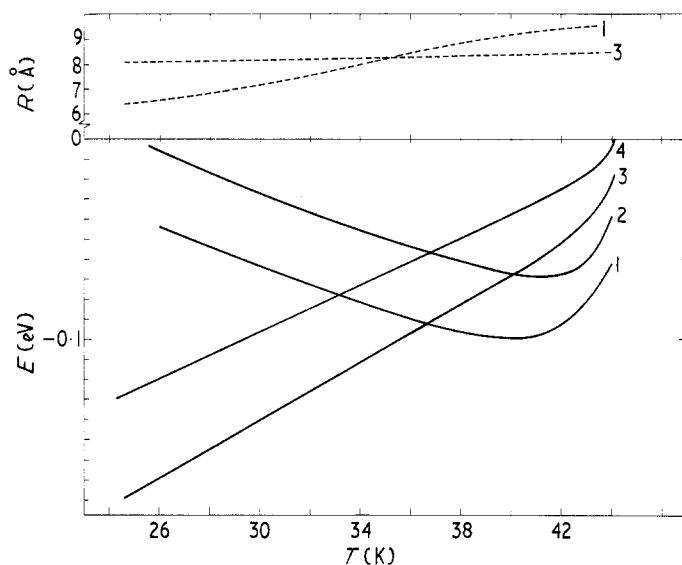


Figure 2. Temperature dependence of E (full curves) and of the radius of the electronic bubbles (broken curves), at $p = p_v$. Curves 1 and 2 were obtained using $\sigma = \gamma_0 (1 - T/T_0)^b$ with $\lambda = 0.39a_0$ and $\lambda = 0.347a_0$ respectively. Curves 3 and 4 are the same as curves 1 and 2 with $\sigma = \sigma_0 (1 - 2\delta/R)$.

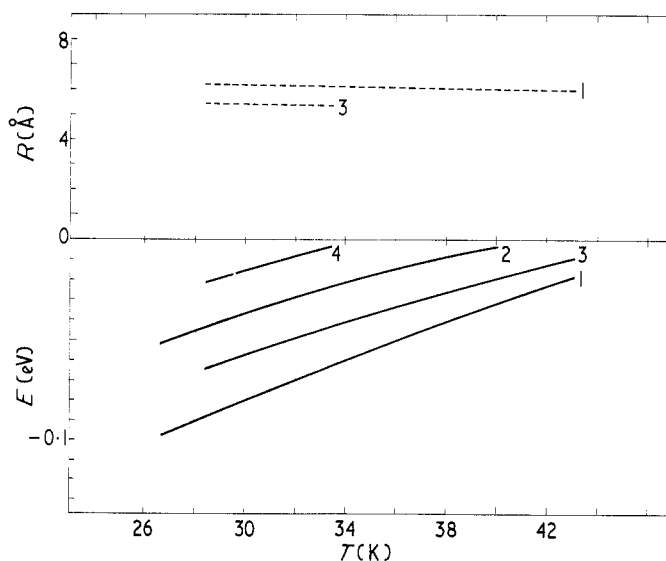


Figure 3. Temperature dependence of E (full curves) and of the radius of the electronic bubble (broken curves) at high pressure, using $\sigma = \sigma_0 (1 - 2\delta/R)$. Curves 1 and 2 obtained at $p = 145.8$ atm., with $\lambda = 0.39a_0$ and $\lambda = 0.347a_0$ respectively. Curves 3 and 4, same as curves 1 and 2 with $p = 242.21$ atm.

high pressures the volume energy $E_v = \frac{4}{3}\pi R^3 p$ becomes a significant contribution to the total energy and is thus responsible for the delocalization. Unfortunately, the existing mobility of excess electrons in liquid neon were taken only at vapour pressure and at temperatures lower than 43 K, ie in the range of T and p where no transition, according to this model, occurs. It would be very interesting to measure the mobility at higher pressures and temperatures, since our results indicate that the pressure necessary to delocalize an electron in neon is not very high, and certainly it is much lower than the melting pressure, at least when T is near T_c . For example at $T = 44.09$ K the critical pressure is about 30 atm if $\lambda = 0.347a_0$ and about 40 atm if $\lambda = 0.39a_0$. The value of pressure at which the delocalization occurs depends strongly on λ , and thus mobility measurements can provide useful information on the nature of the bubble only if supplemented by direct experimental determinations of E_0 , related to λ by equation (3).

A final point to be made is that we get a bubble radius which, at $p = p_v$, increases with temperature in a much slower way than the one calculated by Miyakawa *et al* (1969) (see figure 2). This same radius remains constant at high pressure. Moreover, the upper part of figure 4 suggests that, at a given T , the mobility should be almost constant with pressure, the increase in density being balanced by the decrease of the bubble radius.

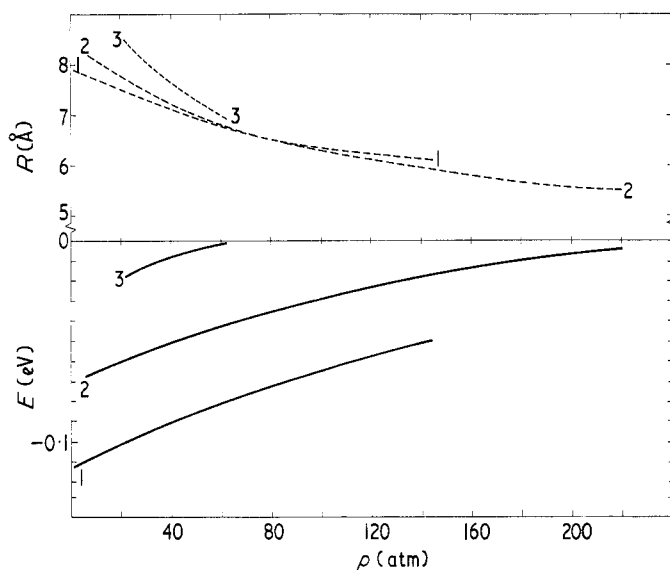


Figure 4. Pressure dependence of E (full curves) and R (broken curves) using $\lambda = 0.347a_0$ and $\sigma = \sigma_0 (1 - 2\delta/R)$. Curves 1 obtained at $T = 27.17$ K, curves 2 at $T = 35.07$ K and curves 3 at $T = 43.11$ K.

We must notice at this point that, from the experimental point of view, the temperature dependence of the bubble radius is by now an open question. The conventional way of obtaining the radius R of the electron-bubble complex is to relate it to the mobility μ by using Stokes formula

$$\mu = \frac{e}{\alpha\eta R} \quad (12)$$

where η is the viscosity of the liquid, e the electron charge and α a constant with a value between 4π and 6π .

The mobility data obtained by Loveland *et al* (1972) predict a bubble radius increasing with temperature in reasonable agreement with the theoretical values obtained by Miyakawa *et al* (1969).

On the other hand, as shown in figure 5, the experimental data given by Bruschi *et al* (1972) suggest that the radius of the bubble at $p = p_v$ should be rather insensitive to

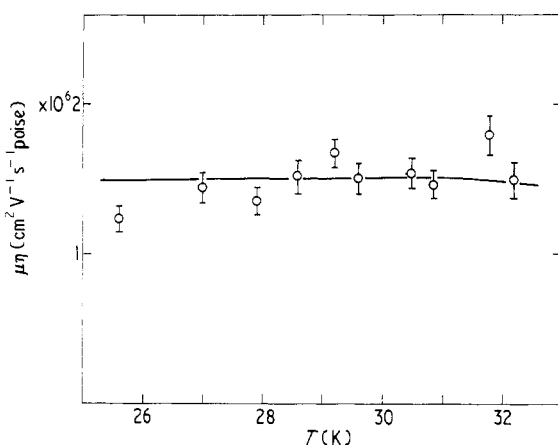


Figure 5. $\mu\eta$ plotted against temperature for $25 \text{ K} \leq T \leq 33 \text{ K}$. Experimental points according to Bruschi *et al* (1972). Solid line is obtained from equation (12) with $\alpha = 4.27\pi$ and R as evaluated from equation 1 with $\sigma = \sigma_0 (1 - 2\delta/R)$.

temperature, in agreement with our prediction. On the basis of the existing mobility data and Stokes law, it is thus impossible to decide whether or not the radius of the bubble in neon at $p = p_v$ exhibits strong variations with temperature.

Summarizing, the simple model used in this paper shows that a bubble collapse can occur in liquid Ne at temperatures near T_c with a few atmospheres of overpressure. Of course in order to give the precise parameters of this transition one should correct the model to take into account electrostriction and polarization effects in a better way. We hope however that the results reported in this paper may give useful hints on how to plan future experimental work aiming at a deeper understanding of the nature and the behaviour of localized electron states in liquid neon.

References

- Bruschi L, Mazzi G and Santini M 1972 *Phys. Rev. Lett.* **28** 1504-5
- Gibbons R M 1969 *Cryogenics* **9** 251-60
- Holleran E M 1971 *Cryogenics* **11** 19-21
- Johnson V I 1960 *A compendium of the properties of materials at low temperature (Phase I), Part I* (NBS)
- Jortner J, Kestner N R, Rice S A and Cohen M M 1965 *J. chem. Phys.* **43** 2614-24
- Levine J L and Sanders T M 1967 *Phys. Rev.* **154** 138-49

- Lippold H 1969 *Cryogenics* **9** 112–4
Loveland R J, Le Comber P G and Spear W E 1972 *Phys. Lett.* **39A** 225–6
Miyakawa T and Dexter D L 1969 *Phys. Rev.* **184** 166–72
O'Malley T F 1963 *Phys. Rev.* **130** 1020–9
Reiss M, Frisch M L, Helfand E and Lebowitz J L 1960 *J. chem. Phys.* **32** 119–24
Springett B E, Cohen M and Jortner J 1967 *Phys. Rev.* **159** 183–90
Springett B E, Jortner J and Cohen M 1968 *J. chem. Phys.* **48** 2720–31
Thompson D G 1966 *Proc. R. Soc. A* **294** 160–74