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Stability of Electronic Bubbles in Liquid Neon and Hydrogen*

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A calculation is performed for the ground-state energies of electronic bubbles in liquid neon and hydrogen as a function of temperature, with the use of (a range of) experimentally determined electron scattering cross sections. It is concluded that bubbles can exist in liquid hydrogen and possibly also in liquid neon at elevated temperatures. Maximum stability would be achieved at about 40° K, but experimental scattering data for Ne are still too uncertain to allow a definite prediction. Electronic bubbles in hydrogen are predicted to contain bound excited states, and excitation energies are computed. Comparison is made with an earlier treatment for liquid neon and hydrogen near their melting points, based on a different approach to polarization effects, and significant errors in that work are corrected.

I. INTRODUCTION

Electronic bubbles in liquid helium have been widely studied, both as a tool in the investigation of excitations of the liquid, and also as one of the most peculiar imperfections in condensed matter.[1,2] This work has shown that the lowest-energy configuration of an extra electron in liquid helium is in the form of a spherical cavity of radius 15–20 Å, the "bubble" being maintained by the zero-point kinetic energy of the electron against the pressure-volume and surface energies which tend to contract it. The surface tension of liquid helium is small (~0.36 erg/cm^2) because of the low van der Waals attraction among the relatively unpolarizable He atoms. The potential well giving rise to the bound state of the electron exists because of the (Pauli principle) repulsion between the electron and the He atoms. That is, atomic helium has a positive scattering length for electrons of $1.2a_0$,[3] giving rise to a well depth of about 1.0 eV,[4] where a_0 is the Bohr radius.

There exist other nonpolar liquids in which electronic bubbles might occur, and in which bubbles might be investigated under convenient experimental conditions. A general criterion for the stability of bubbles in such materials near their melting points has been given[5] in terms of the liquid density, surface tension, atomic polarizability, and atomic scattering cross section for low-energy electrons, the latter evaluated in the (hypothetical) absence of atomic polarization. Clearly, a liquid is required in which the constituents repel an electron, and which has a small surface tension. The surface tension of the rare-gas liquids increases with atomic number (and polarizability), and the electron affinity of the atoms likewise increases, the scattering length becoming negative for argon and heavier rare-gas atoms. Thus, only neon remains as a possible host for bubbles among the rare-gas liquids. Its atomic polarizability is about twice that of helium, hence, its surface tension is several times as large, and its experimental scattering length is substantially smaller than that of helium. Nevertheless, the latter is positive, and bubbles surrounding positronium have been observed in liquid neon,[6] so it seemed worthwhile to investigate the possibility of bubble existence in this medium.

The other obvious possibility is liquid hydrogen, which appears intermediate between He and Ne from the standpoint of surface tension and even better than He as regards scattering length, though the polarizability is greater than either He or Ne. Bubbles have been observed around positronium in this liquid also,[6] and there are strong indications that electronic bubbles also exist.[7] Accordingly, we undertook a theoretical investigation of bubbles in liquid H_2 and Ne to test their stability under the conditions which prevail experimentally at various temperatures.

Springett, Jortner, and Cohen,[5] have discussed these liquids (*inter alia*) near their melting points from a different point of view as regards the treatment of polarization. In the case of neon, the conclusions appear to differ qualitatively; numerical errors in Ref. 5 are responsible for this apparent discrepancy. A corrected version of the treatment of Ref. 5 is in agreement with our results, to the effect that the stability of the electronic bubble in neon is marginal. Correction of numerical errors in the treatment of Ref. 5 for hydrogen leads to an increased stability (by a factor of about 3), and according to that revised treatment and the present one, the stability of electronic bubbles in liquid hydrogen is even greater than in liquid helium.

II. CALCULATIONS AND RESULTS

The following is an extremely simple model which has apparently been adequate for the treatment of bubbles in liquid He: Around an electron localized within a liquid, the number density of atoms (or molecules) makes an abrupt change at some radius R, the density being zero inside the cavity and equal to the equilibrium density n outside the sphere. The potential energy within the cavity is taken to be a constant $-E_0$ with respect to that in the liquid. This model yields results in good agreement with the results of a more refined calculation in the case of liquid He.[2]

E_0 can be estimated from a pseudopotential calculation as was done for helium, and one of us (T.M.) has performed such a calculation for neon.[8] If we use Born approximation without polarization effects included, E_0 becomes $E_0(B,$ no pol.), equal to the minimum average energy for a free electron in a liquid, or simply the average over space of the pseudopotential $V_{\text{ps}}(r)$ multiplied by the average density of the liquid

$$E_0(B, \text{ no pol.}) = n \int V_{\text{ps}}(r)\, d\tau .$$

For neon, this gives us $E_0 = 1.82$ eV at 24.55 °K, which is even larger than the corresponding value for He at 1.3 °K (1.26 eV).[2] However, the effect of polarization is much more important for neon and for hydrogen than for helium, and cannot be ignored even in a first approximation. This fact is demonstrated by the smallness of neon's experimental electron scattering length.[3] As a result, the total effective potential is determined by a balance between the repulsive and polarization potentials (see Fig. 1), and its accurate calculation from first principles will be very difficult, since the dominant contribution to the polarization comes from continuum states of the neon plus electron system. Another effect of polarization is to lower the energy of the electron localized in the well, as will be described below.

Accordingly, we compute the well depth from a Wigner-Seitz and from an optical-model calculation. In the Wigner-Seitz approximation, we replace an atom (or a molecule) by a hard sphere of radius l, equal to the low-energy electron scattering length, and assume that these atoms are arranged in a periodic array with a Wigner-Seitz equivalent sphere radius r_s given by

$$r_s = (3/4\pi n)^{1/3} .$$

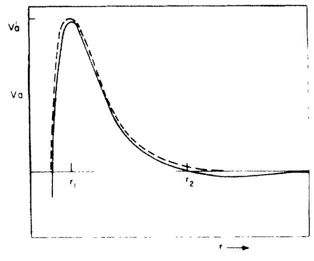

FIG. 1. Schematic dependence of the electron-atom potential V_a on distance r, the solid line including the effect of polarization, and the dashed line without polarization. The maximum of the dashed line corresponds to $r_1 = 1.2a_0$ and $V_a' = 9.5$ eV for an s-like electron wave function; r_2 is estimated to be $3.2a_0$ (see Ref. 8) in the case of neon.

The lowest energy of a nonlocalized electron is that for which the s-like wave function of the electron around a hard-sphere atom of radius l can be joined smoothly onto the wave functions in the neighboring "spherical cells" of radius r_s, i.e., that for which

$$\frac{d}{dr}\left[\frac{\sin k(r-l)}{r}\right]_{r_s} = 0.$$

This boundary condition yields a condition for the wave number k_0 of the electron,

$$k_0 r_s = \tan k_0 (r_s - l), \tag{1}$$

and from the smallest positive value of k_0 the minimum energy or the energy barrier E_0 can be computed by the relation

$$E_0 = \hbar^2 k_0^2 / 2m . \tag{2}$$

Alternatively, in the optical approximation,[2] one takes the multiple scattering into account by introducing the t matrix, the diagonal matrix element of which for an exact wave function $|0\rangle$ of the electron in the limit of zero energy is related to the scattering length l by

$$\langle 0 | t | 0 \rangle = \hbar^2 l / 2m .$$

From this matrix element we get the well depth

$$E_0 = 4\pi n \langle 0 | t | 0 \rangle = 4\pi n \hbar^2 l / 2m . \tag{3}$$

(As the increase in the electron's kinetic energy is not taken into account, this method gives an underestimate for the value of E_0.) Thus, in both treatments, knowledge of the scattering length allows the determination of the well depth in the approximation that this single parameter suffices to describe the electron-atom interaction.

Thompson[9] carried out a phase-shift calculation for electron scattering by atomic neon (and argon) including the effect of polarization in a modified Temkin approximation.[10] From the circumstance that his computed cross sections for neon were somewhat larger than some experimental values, he estimated that only 80% of the polarization effect is included in his calculations. The scattering length deduced from his calculation is $l = 0.347a_0$.

Experimentally, the situation for neon is the most uncertain among rare-gas atoms. Because of the small value of the scattering length, evidently as a result of cancellation between repulsive and polarization interactions, the experimental values of scattering length show a large scatter and range from 0.03 a_0 to $0.39a_0$; the values $0.24a_0$ and $0.39a_0$ seem most representative.[3]

As a result the value of E_0 also varies according to which of the values for the scattering length is chosen. In Fig. 2, we show the temperature (through density) dependence of E_0 for two values of the scattering length l, determined according to Eqs. (1)-(3).

For the hydrogen molecule, Wilkins and Taylor[11] computed by an iterative method a low-energy electron scattering cross section which is in good agreement above 0.02 eV with the experimental data by Golden, Bandel, and Salerno, and by Bekefi and Brown.[12] (In this calculation, the polarization effect was not taken into account. The general agreement with experiment led Wilkins and Taylor to the conclusion that the polarization effect cannot be large.) These experimental results extrapolated to zero energy by the method of O'Malley *et al.*[13] give $l = 1.25a_0$, whereas another experiment[14] leads to the value $l = 1.51a_0$.

The polarizability of the hydrogen molecule is larger than that of atomic neon, this fact suggesting that the effect of polarization is also important in this case. Further, the molecule is not spherical and the polarizability exhibits anisotropy[15] perpendicular and parallel to the molecular axis

$$\alpha_{\perp} = 0.714 \times 10^{-24}\,\text{cm}^3, \qquad \alpha_{\parallel} = 1.028 \times 10^{-24}\,\text{cm}^3.$$

Therefore, a hydrogen molecule would tend to align its axis parallel to the radius vector connecting its center of mass with the electron in the bubble, presumably lowering the value of the effective repulsive potential for the electron thereby. That is, the scattering experiments in the gas perform an average over orientations, but around a bubble only the lowest-energy configurations would be expected to occur. As a first approximation, we ignore this anisotropy, presumably overestimating E_0.

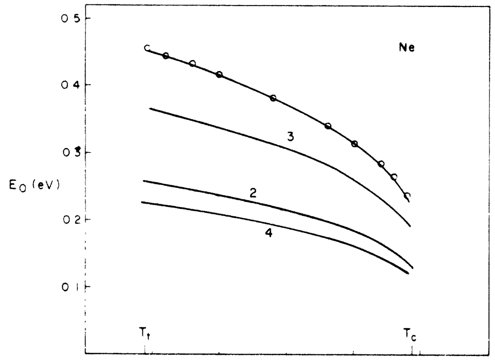

FIG. 2. Temperature dependence of the barrier height E_0 in liquid neon. Curves 1 and 2 correspond to the Wigner-Seitz method with scattering lengths $0.39a_0$ and $0.24a_0$, respectively. Curves 3 and 4 result from the optical approximation with $l = 0.39a_0$ and $0.24a_0$, respectively. The open circles are derived from Ref. 5, corrected as discussed in the text.

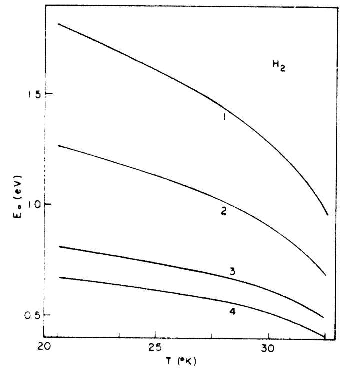

FIG. 3. Temperature dependence of the barrier height E_0 in liquid hydrogen. Curves 1 and 2 correspond to the Wigner-Seitz method with l equal to $1.51a_0$ and $1.25a_0$, respectively; curves 3 and 4 result from the optical approximation with $l = 1.51a_0$ and $1.25a_0$, respectively.

By the Wigner-Seitz and optical approximations, we made estimates of the well depth in liquid hydrogen at several values of the temperature, for both experimental values of l, with the results shown in Fig. 3.

As shown in Fig. 1 and in the discussion above, the polarizability of the molecules of the liquid acts to reduce the value of the barrier E_0, which may be viewed as the kinetic energy an electron at infinity would require in order to penetrate the liquid. However, an electron at the center of a cavity of radius R in a medium of dielectric constant K will have its field energy changed (reduced) by an amount indicated in Fig. 4

$$E_K = -\,[(K-1)/K]e^2/2R. \tag{4}$$

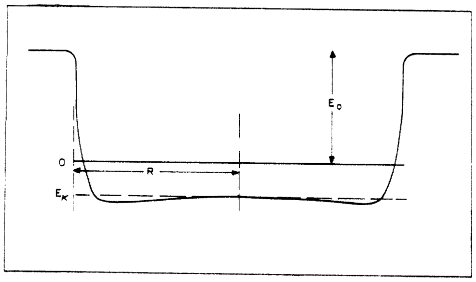

FIG. 4. Schematic representation of the potential energy for an electron in a cavity. E_0 is the barrier height, and E_K [see Eq. (4)] is the polarization energy at the center of the bubble.

In liquid He, E_K is only -0.02 eV at the equilibrium radius and can be ignored, but for neon and hydrogen it is of order -0.1 eV at equilibrium and represents a sizable correction, particularly in view of the small barrier E_0 for neon. Calculations with the pseudopotential and polarization potential for neon indicate that the variation of potential energy within the cavity is small (~0.03 eV); this variation will be neglected in favor of the convenience of dealing with a square-well potential.

This treatment of polarization effects differs from that of Ref. 5. In that work, the atomic scattering cross section was calculated without the inclusion of polarization effects, a Wigner-Seitz calculation was performed with a fictitious rigid (unpolarizable) atom scattering length substantially larger than the experimental value, thus resulting in a larger k_0 and kinetic energy than above, and this result was reduced by a polarization energy computed for the liquid. The resulting well depths were estimated to be 0.75 and 0.9 eV (1.1 eV) for neon and hydrogen (deuterium), respectively, to be compared with those exhibited in Figs. 2 and 3 near 25 and 20 °K, respectively. Correction of numerical errors in Ref. 5 changes these well depths to 0.46 and 2.2 eV, respectively.

This approach was not taken in this paper for the following reasons: (i) The screening of polarization (or the local field effect) is smaller for neon (~10%) than for argon (more than 20%). (ii) In contrast to the case of argon, in which the polarization potential makes a dominant contribution to the scattering length in the zero energy limit, the effect of polarization on the scattering length by neon is more difficult to estimate in a reliable way, and larger error will be expected in such an estimate. (iii) The value of scattering length calculated by Thompson[9] taking into account about 80% of the polarization effect ($0.374a_0$) is well within the scatter of experimental values (the largest one being $0.39a_0$).

Therefore, it does not seem to be practical or convincing to make estimates of the various terms, which may be in error by more than 10%, and then to take the difference of these to estimate the value of E_0. Rather we preferred to take a larger range of values for the scattering length l. The values of E_0 for neon estimated according to the method of Ref. 5 (after correction of numerical errors) agree with our values, as will be seen, for the larger of the experimental scattering lengths.

A term similar to Eq. (4) was also derived in Ref. 5, but was neglected in the stability criterion in view of the large values of E_0. In our treatment of neon, the term E_K is important in obtaining stability, as shown below.

In the square-well potential, of depth $E_0 + e^2(K-1)/2KR$ we have computed $E_e(E_0, K, R)$, the lowest-energy ($1s$) eigenvalue for a localized electron as a function of R. The dielectric constants for liquid Ne[16] and H_2[17] were taken from the literature and scaled with density for different temperatures according to the Lorentz-Lorenz relation.

The total energy change upon localizing an excess electron within the cavity at temperature T consists of five terms

$$\Delta(R, P, \sigma, K, E_0) = E_e + E_s + E_p + E_K - E_0. \qquad (5)$$

The condition for stability of bubbles is that Δ be negative. $E_S(R, \sigma)$ and $E_p(R, P)$ are, respectively, the surface and pressure energies which are the work done against surface tension $\sigma(T)$ and the pressure $P(T)$

$$E_s = 4\pi\sigma R^2, \quad E_p = \tfrac{4}{3}\pi R^3 P.$$

Note that E_0, K, and σ depend on the density, and therefore change with T, as does the equilibrium vapor pressure. It should be emphasized that all our calculations are performed for values of E_0, σ, K, and P consistent with equilibrium conditions at temperature T.

Liquid densities and equilibrium vapor pressures were taken from the literature.[18, 19] In some cases, interpolated or extrapolated values were used (without significant error, we believe).

For the surface tension we used "experimental" bulk values computed from the temperature dependence

$$\sigma(T) = \sigma_0(1 - T/T_c)^b \ \text{erg/cm}^2,$$

with $\sigma_0 = 15.20$, $T_c = 44.38$ °K, and $b = 1.216$ for neon,[20] and $\sigma_0 = 6.1$, $T_c = 33.24$ °K, and $b = 1.23$ for hydrogen.[21] This formula is known to give a good fit to the experimental data for heavier rare-gas liquids.[22] Of course, this law of corresponding states may not be a good approximation in neon and hydrogen, but the above formula fits the experimental data for hydrogen up to temperatures close to T_c. Unfortunately, the range of temperature over which the surface tension of neon is measured is limited, and we cannot assess the accuracy of the formula in this case.

Knowing all the terms in Eq. (5), we may minimize Δ with respect to R so as to find the optimum value of $R, R_{\min}$, as a function of T. This procedure was carried out using for E_0 the values shown in Figs. 2 and 3 computed by the Wigner-Seitz method for the two indicated values of the scattering length, and the results for neon and hydrogen are shown in Figs. 5 and 6, respectively. In these figures, T_t and T_c are the triple points and critical temperatures.

Inspection of Fig. 6 shows that for either value of scattering length of H_2, the bubble is stable at all temperatures of the liquid, stabler and smaller

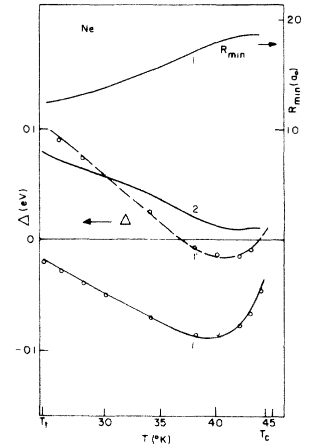

FIG. 5. Temperature dependence of Δ and equilibrium radius of an electron bubble in liquid neon. Curves 1 and 2 correspond to the results of the Wigner-Seitz calculation shown in curves 1 and 2 of Fig. 2, respectively. Curve 1′ results from omitting E_K of Eq. (4). The open circles correspond to those of Fig. 2, with and without the inclusion of E_K.

than in liquid helium. The value of Δ near 20 °K obtained by the corrected version of Ref. 5 is approximately − 1.9 eV, about − 0.6 eV with the original well depth. (The value of kinetic energy T in Ref. 5 should be changed from 2.0 to 3.60 eV, and the polarization energy U_p should be changed from − 1.1 to − 1.38 eV, and the total from 0.9 to 2.2 eV). Neglect of the term E_K in Eq. (4) is seen to decrease the absolute magnitude of Δ by about 0.1 eV, and increase the bubble radius by about 2 a_0.

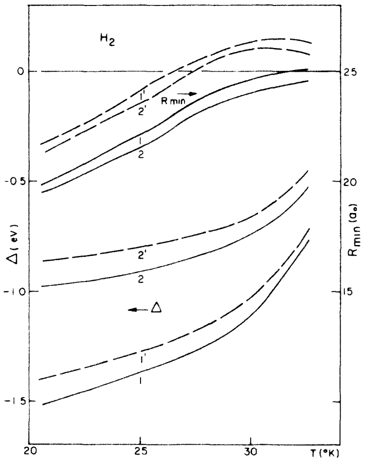

FIG. 6. Temperature dependence of Δ and equilibrium radius of an electron bubble in liquid hydrogen. Curves 1 and 2 are based on the Wigner-Seitz calculation of curves 1 and 2 of Fig. 3. The dashed curves result from the omission of E_K of Eq. (4).

Because of the large values of surface tension at low temperature, and small values of barrier height, the bubbles in neon are barely stable or unstable. Although the electronic part of the energy difference $E_e + E_K - E_0$ increases as the temperature is raised, the surface tension decreases its value more rapidly. Thus, the higher the temperature the more favorable are conditions for bubble formation until, above about 40 °K, the increase in $E_p + E_K$ more than compensates for the decrease in E_S.

The lowest-energy curve, labeled 1 in Fig. 5, is computed with a well depth E_0 taken from curve 1 in Fig. 2, equal to 0.46 eV at low temperatures. It is clear that an increase of well depth to 0.75 eV, as deduced in Ref. 5, would give rise to stable bubbles at all temperatures, with an energy below the range of this figure. However, there is a numerical error of 0.27 eV in the evaluation of the polarization potential in Ref. 5. (Instead of − 1.17 eV in Table I of Ref. 5, it should be − 1.44 eV. The kinetic energy should also be changed from 1.92 to 1.90 eV.) We have repeated the calculation for neon by the method of Ref. 5 with the results shown by open circles in Figs. 2 and 5. The agreement with the calculated curve for a scattering length $l = 0.39a_0$ may lend support to this larger value of l.

An electron-injection experiment should readily settle the question of stability in neon. It is entirely possible, if the energy should lie between curves 1 and 2 of Fig. 5, that the mobility of an electron will be found to be large at low and high temperatures, exhibiting a sharp minimum (a decrease of several orders of magnitude) near 40°K where bubbles are stable.

For comparison only, we note that the measured radii of the positronium bubbles[6] at the normal boiling points in Ne and H_2 are $18.5a_0$ and $24.5a_0$, respectively, as contrasted with our calculated values for the electronic bubble of about $18a_0$ and $20a_0$, respectively, at the temperatures of their greatest stability. (Positronium is neutral, of course, and polarization effects are less pronounced. Furthermore, different scattering lengths are involved, so that one would not expect equal bubble radii.)

In the case of liquid neon, even at the most stable predicted configuration at 40 °K, there exists no bound excited state. For liquid hydrogen, there do exist bound excited states. Figure 7 portrays two configuration coordinate diagrams, based on the parameters leading to curves 1 and 2 in Fig. 6 at $T = 20.5$ °K, as described for electronic bubbles in liquid helium by Fowler and Dexter.[1] For scattering length $1.51a_0$, the $2p$ state is bound at all temperatures. For $l = 1.25a_0$, it merges with the continuum at low and high T, being bound between about 23 and 31 °K.

The coordinate R is meaningful for s states,

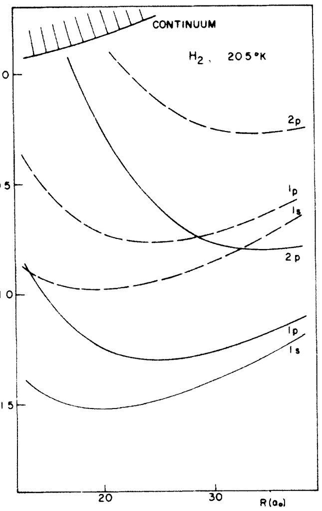

FIG. 7. Configuration coordinate diagram for electronic bubble in liquid hydrogen, exhibiting the ground (1*s*) and excited *p* states according to the Wigner-Seitz calculation leading to curves 1 and 2 in Fig. 3. The solid curves are for $l = 1.51a_0$, the dashed curves for $l = 1.25a_0$.

being just the radius of the spherical bubble. The calculations for *p* states are also performed in a spherical potential. There would actually be expected to occur a nonspherical Jahn-Teller distortion which would lower the energy further. This point is discussed by Fowler and Dexter[1] for the generally similar case of bubbles in liquid helium.

Figure 8 exhibits the predicted 1*s* → 1*p* and 1*s* → 2*p* excitation energies as a function of *T* for electronic bubbles in liquid hydrogen for the larger value of scattering length $l = 1.51a_0$. It also shows the 1*p* → 1*s* emission energies predicted following a (hypothetical) spherical relaxation. (Since no Jahn-Teller distortion has been allowed for, these emission energies are not to be considered as realistic.) The curves dealing with the 1*p* state are essentially the same for the smaller scattering length ($1.25a_0$), and it seems safe to predict an intense absorption line at 0.27 eV near 20 °K, decreasing to 0.18 eV at high temperatures.

The oscillator strength for the 1*s* → 1*p* transition of the electronic bubble in liquid hydrogen is predicted to be 0.971, 0.025 for the 1*s* → 2*p* transition, near 20 °K, on the assumption of the larger scattering length. These figures compare with 0.97 and 0.025 for liquid helium. (For the smaller scattering length the strengths are 0.975 and 0.023.)

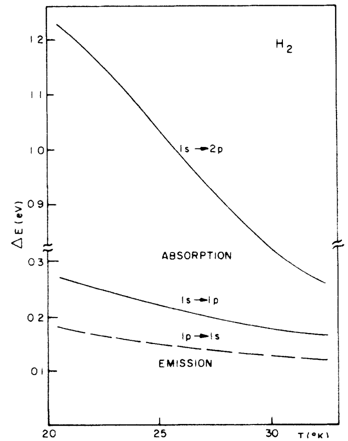

FIG. 8. Transition energies for absorption 1*s* → 1*p* and 1*s* → 2*p* and emission 1*p* → 1*s* of electronic bubbles in liquid hydrogen as a function of temperature. The solid and dashed curves are for $l = 1.51a_0$ and $1.25a_0$, respectively.

Finally, we comment on possible sources of error in these calculations. First, we have used the macroscopic value of the surface tension throughout, and ignored the curvature and structure of the surface of the cavity. A much more detailed theory would be required to eliminate these simplifications. Secondly, our treatment of polarization effects is only approximate, since we have used the total free-atom scattering length, which includes polarization for the free atom, and have not corrected the well depth (except for E_K) for a change in polarization in the liquid resulting from overlap in the polarization fields of the environment. This effect exists, and is important in the case of liquid argon.[23] For hydrogen we believe that these possible errors will not change qualitatively the conclusion that electronic bubbles can occur. In the case of neon, the uncertainty arising from that of the experimental atomic scattering length is amplified by these considerations, and can best be resolved by experiment.

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[1] J. Wilks, The Properties of Liquid and Solid Helium (Oxford University Press, London, 1967); see also references contained in W. B. Fowler and D. L. Dexter, Phys. Rev. 176, 337 (1968).

[2] J. Jortner, N. R. Kestner, S. A. Rice, and M. H. Cohen, J. Chem. Phys. 43, 2614 (1965).

[3] T. F. O'Malley, Phys. Rev. 130, 1020 (1963).

[4] M. A. Woolf and G. W. Rayfield, Phys. Rev. Letters 15, 235 (1965).

[5] B. Springett, J. Jortner, and M. Cohen, J. Chem. Phys. 48, 2720 (1968).

[6] C. V. Briscoe, S. I. Choi, and A. T. Stewart, Phys. Rev. Letters 20, 493 (1968).

[7] B. Halpern and R. Gomer, J. Chem. Phys. 43, 1069 (1965).

[8] T. Miyakawa (to be published). Neon will be included in a paper containing the pseudopotentials for a number of alkalis, halogens, and rare gases.

[9] D. G. Thompson, Proc. Roy. Soc. (London) A294, 160 (1966).

[10] A. Temkin, Phys. Rev. 107, 1004 (1957); 116, 958 (1959).

[11] R. L. Wilkins and H. S. Taylor, J. Chem. Phys. 47, 3533 (1967).

[12] D. E. Golden, H. W. Bandel, and J. A. Salerno, Phys. Rev. 146, 40 (1966); G. Bekefi and S. C. Brown, *ibid.* 112, 159 (1958).

[13] T. F. O'Malley, L. Spruch, and L. Rosenberg, J. Math. Phys. 2, 491 (1961).

[14] This value is based on the experimental data of A. U. Englehardt and A. V. Phelps, Phys. Rev. 131, 2115 (1962).

[15] W. Kolos and L. Wolniewicz, J. Chem. Phys. 43, 2429 (1964); N. J. Bridge and A. D. Buckingham, *ibid.* 40, 2733 (1964); Proc. Roy. Soc. (London) A295, 334 (1966).

[16] L. Bewilogwa, A. Handstein, and H. Hoegen, Cryogenics 6, 21 (1966).

[17] R. Landoldt and W. Bornstein, Zahlenwerte und Funktionen (Springer-Verlag, Berlin, 1959), 6th ed. II Band 6-Teil, p. 605.

[18] G. A. Cook, Argon, Helium, and the Rare Gases, (Wiley-Interscience, Inc., New York, 1962).

[19] R. Landoldt and W. Bornstein, Zahlenwerte und Funktionen (Springer-Verlag, Berlin, 1950), 6th ed.

[20] F. B. Sprow and J. M. Prausnitz, Trans. Faraday Soc. 62, 1097 (1966).

[21] Yu. P. Blagoi and V. V. Pashkow, Zh. Eksperim. i Teor. Fiz. 49, 1453 (1965); [English transl.: Soviet Phys. – JETP 22, 999 (1966)].

[22] B. L. Smith, P. R. Gardner, and E. H. C. Parker, J. Chem. Phys. 47, 1148 (1967).

[23] J. Lekner, Phys. Rev. 158, 130 (1967).

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Time Correlations and Conditional Distribution Functions for Classical Ensembles of Free Rotors*

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Explicit expressions are obtained for the classical rotational time-correlation functions for free rotation of the following: the linear, spherical-top, and symmetric-top molecule. This is done by deriving the eigenfunctions and eigenvalues of the potential-free rotational Liouville operator for each case. Conditional distribution functions for orientations and angular momenta are then constructed, and correlation functions are computed by evaluating phase-space averages with the distribution functions. The results obtained agree with those of Sears for the linear molecule and Steele for the spherical top, but differ somewhat from the calculation of Agrawal and Yip for the symmetric top molecule. The reason for this discrepancy is discussed briefly.

I. INTRODUCTION

In classical statistical mechanics the behavior in time of a system point in phase space is governed by Liouville's equation,

$$\frac{dW}{dt}=0 \qquad (1)$$

$$=\frac{\partial W}{\partial t}+i\mathcal{L}W\ , \qquad (2)$$