

TABLE IV: Estimates of the Influence of $\Lambda_1 F$ on Y

$F, V/cm$	2000	4000	6000
Set 1 ^a			
$\Lambda_1, \text{\AA}$	140	140	140
$\Lambda_1 F$	2.80×10^{-3}	5.6×10^{-3}	8.4×10^{-3}
$Y(E_i=0.1)$	0.23	0.28	0.32
Set 2			
$\Lambda_1, \text{\AA}$	70	70	70
$\Lambda_1 F$	1.4×10^{-3}	2.4×10^{-3}	4.2×10^{-3}
$Y(E_i=0.1)$	0.21	0.225	0.25
Set 3			
$\Lambda_1, \text{\AA}$	280	290	290
$\Lambda_1 F$	5.6×10^{-3}	11.2×10^{-3}	16.8×10^{-3}
$Y(E_i=0.1)$	0.28	0.365	0.46

^a Best fit of experimental data by distribution f_1 .

Furthermore, it could be seen that A_2 depended only weakly on N . We are led to conclude that at the LAr density A_2 is a function of $\alpha_{LAr} = \Lambda_1 F/E$ only. Although we do not know the exact dependence of $p(E_i, F)$ on A_2 we may assume that α_{LAr} is the physical quantity relating the influence of Λ_1 and F on $p(E_i, F)$ or, in other words, $p(E_i, F)$ is a function of α_{LAr} only. In order

to estimate the influence of the variation of Λ_1 on $p(E_i, F)$, we plotted $(R_{LAr}/R_{vac})^{0.5}$ as a function of α_{LAr} . A straight line was obtained

$$Y = (R_{LAr}/R_{vac})^{0.5} = 0.185 + 16\Lambda_1 F \quad (16)$$

We do not know how $Y(\alpha_{LAr})$ will behave for small and large α values, but taking the linear approximation we find the following variations given in Table IV. Although the variation of Y with Λ_1 is not very pronounced, we see that doubling the value of Λ_1 (set 3) leads to differences between measured values and estimated values especially at 6 kV/cm which are outside of the error limits. Taking a smaller Λ_1 value (set 2) leads to a reduction of Y although less pronounced.

Summarizing, we found that our trajectory model allowed a direct calculation of the photoemission yield in LAr with a set of parameters, which were derived from mobility data by means of Lekner's model. Variation of Λ_1 by more than a factor of 2 (or $1/2$) leads to discrepancies between the calculated and observed yields. This means that the chosen values of Λ_1 and Λ_0 , obtained from mobility data, are applicable to Tauchert's experiments and that large deviations in these values would lead to internal inconsistencies.

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Electron Mobility Calculations in Liquid Xenon by the Method of Partial Waves

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The method of partial waves in the framework of the fluctuation model has been applied to describe the density dependence of the electron mobility in liquid xenon. The limiting factor in the transport of excess electrons in such systems can be attributed to their scattering due to density fluctuations. Instead of the usual Born approximation we handled the scattering problem with the more general method of partial waves. This made it possible to work out the average fluctuation size from the transport data. Calculations were carried out in the density range $(6.7-11.5) \times 10^{21}$ atoms/cm³. Good agreement with measured mobility curves can be obtained by considering reasonable values for the average fluctuation size.

1. Introduction

The relatively high mobility of excess electrons in insulating liquids such as some hydrocarbons, argon, krypton, and xenon is a fascinating challenge for theoreticians. Just as in the theory of liquid metals,¹ the main question involves the existence and description of the quasifree state in view of the lack of translational symmetry in the liquid. Nevertheless insulating liquids differ remarkably from liquid metals because of their different band structure, mostly due to the presence of a band gap in the insulators. The mobility of a quasifree electron is governed by the scattering mechanisms which limit its drift velocity to a relatively small value. The search for possible scattering mechanisms made it clear that considering a single atom or molecule as a scattering center leads to a limited understanding of the conduction phenomena. In contrast to this single scatterer approximation, especially at higher densities multiple scattering must play an important role.

Electron mobility calculations have been carried out in liquid hydrocarbons by Berlin, Nyikos, and Schiller with the fluctuation model² and by Basak and Cohen in liquid argon with the deformation potential model.³ Both theories account for the multiple scattering of the quasifree electrons in a similar manner, namely, using a spherical potential derived from the density fluctuations

of the liquid. This potential can be visualized as a perturbation of the energy of the bottom of the conduction band, ΔV_0 , rather than some kind of superposition of interaction potentials from individual particles. This perturbation energy can be expanded in a series in terms of density fluctuation. Both theories then handle the scattering problem with the aid of the Born approximation and are restricted to the vicinity of the mobility maximum.

In order to describe many other hydrocarbons, helium, neon, and hydrogen another electronic state has to be considered, a slowly moving localized state with a mobility comparable to that of heavy ions. This state can be understood in terms of the Springett, Jortner, and Cohen theory of electronic bubbles.⁴ A further question arises about the mechanism of formation of such localized states in a liquid. Experimental investigation of picosecond dynamics of electron transfer⁵ indicates two possible stages of electron localization, first transition from the quasifree state to a bound state and then relaxation of the liquid structure around the electron. This second process has been recently investigated

(1) J. M. Ziman, *Phil. Mag.*, **6**, 1013 (1961).

(2) Yu. A. Berlin, L. Nyikos, and R. Schiller, *J. Chem. Phys.*, **69**, 2401 (1978).

(3) S. Basak and M. H. Cohen, *Phys. Rev. B*, **20**, 3404 (1979).

(4) B. E. Springett, J. Jortner, and M. H. Cohen, *J. Chem. Phys.*, **48**, 2720 (1968).

(5) G. A. Kenney-Wallace, G. E. Hall, L. A. Hunt, and K. Sarantidis, *J. Phys. Chem.*, **84**, 1145 (1980).

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by Calef and Wolynes as an application of the Schmoluchowski-Vlasov theory.⁶ Not too much is known about the first process, i.e., about the localization before the reorganization of the liquid.

The main aim of the present paper is to extend the fluctuation model beyond the limits posed by the Born approximation. In the next section we recall two sufficient conditions for the applicability of Born approximation. Then we briefly outline the method of partial waves in the framework of the fluctuation model. Section 3 is devoted to the discussion of our mobility calculations in liquid xenon. The results are compared to those we obtained in liquid argon previously. In the Appendix we make a proposal for the description of the first step of the electron localization mechanism.

2. Mobility of Quasifree Electrons by the Method of Partial Waves

The fluctuation model of the quasifree electrons contains three main assumptions. First, the Boltzmann equation can be applied; in other words, there has to be enough time between the scattering events for the electron to reach a momentum eigenstate, otherwise the Kubo formalism should be used. The second assumption lies in the fluctuation model itself. In order to create the scattering potential as a consequence of density fluctuations, a local conduction band energy, $V_0(r)$, and a local density, $n(r)$, have to be defined. The third limitation originates in the application of the Born approximation to describe the scattering process. In a previous paper⁷ we analyzed the implications and consequences of these constraints in the case of several hydrocarbons and liquid argon. It turned out that the strongest bounds are due to the use of the Born approximation. It is convenient to express these bounds as prescriptions for the influence range of the scattering potential, A , either

$$A \gg \frac{m}{4\pi\hbar^2} \left(\frac{\partial V_0}{\partial n} \right)^2 \langle n \rangle^2 \kappa \quad (1)$$

or

$$A \ll \frac{4\pi\hbar^4}{3k_B T m^2} \left(\frac{\partial V_0}{\partial n} \right)^{-2} \langle n \rangle^{-2} \kappa^{-1} \quad (2)$$

where κ and $\langle n \rangle$ are the isothermal compressibility and the number density of the liquid, respectively. In view of the lack of a satisfactory theory for the conduction band energy in an insulating liquid its density derivative, $\partial V_0/\partial n$, is obtainable preferably by the differentiation of measured $V_0(\langle n \rangle)$ curves. These inequalities will obviously hold in the vicinity of the extrema of $V_0(\langle n \rangle)$ functions and break down approaching the critical point, where the isothermal compressibility has a singularity.

The parameter A has another meaning which is more easily related to a measurable quantity. Because the scattering potential is derived from density fluctuations its range is related to the average radius of a fluctuation. This in turn can be related to the correlation length, ξ , in the liquid.

To overcome the limitations created by the Born approximation we replaced it with the more general method of partial waves. The following derivation is straightforward.

If V_0 depends primarily on $\langle n \rangle$, its fluctuation, $\Delta V_0(r)$, can be expressed in terms of local density fluctuations, $\Delta n(r)$:

$$\Delta V_0(r) = \frac{\partial V_0}{\partial n} \Delta n(r) + \dots \quad \text{if } |r| \leq A \quad (3)$$

$$= 0 \quad \text{if } |r| > A$$

When the first derivative $\partial V_0/\partial n$ vanishes, the higher-order terms of the expansion dominate the scattering process. The analytical solution for elastic scattering on this potential is well-known and can be expressed with the phase shifts, δ_l :

$$\delta_l = \arctan \left[\frac{k_j l(k^* A) j_l'(k A) - k^* j_l(k A) j_l'(k^* A)}{k_j l(k^* A) y_l'(k A) - k^* j_l'(k^* A) y_l(k A)} \right] \quad (4)$$

where l is the angular momentum quantum number, j_l and y_l are spherical Bessel functions of the first and second kind, j_l' and y_l' are their derivatives with respect to the argument, $k = (2mE)^{1/2}/\hbar$, and $k^* = (2m(E - \Delta V_0))^{1/2}/\hbar$. Here E denotes the thermal energy of the electrons.

The total scattering cross section is built up from the contributions of individual partial waves:

$$\sigma = \frac{4\pi}{k^2} \sum_{l=0}^{\infty} (2l+1) \sin^2 \delta_l \quad (5)$$

To obtain the mean free path, Λ , for the electrons we have to average over the fluctuations of different Δn

$$\Lambda^{-1} = \frac{1}{(2\pi \langle n \rangle^2 k_B T \kappa V)^{1/2}} \int_0^{\infty} \sigma \exp\left(-\frac{(\Delta n)^2 V}{2 \langle n \rangle^2 k_B T \kappa}\right) d\Delta n \quad (6)$$

where V is the volume of a fluctuation. The form of the exponential shows clearly that the linearized fluctuation formalism was used. This means that this simple version of the theory necessarily breaks down approaching the critical point.

The above-mentioned mean free path still contains an electron energy dependence, so the mobility can be expressed by averaging over the Boltzmann distribution

$$\mu = \frac{2e}{3} \left(\frac{2}{\pi m k_B T} \right)^{1/2} \int_0^{\infty} x \Lambda e^{-x} dx \quad (7)$$

where the notation $x = E/k_B T$ was introduced. In the derivation of this formula the usual form of quasifree density of states has been invoked.

The complicated structure of the integrand in eq 6 and 7 makes it impossible to derive analytic expressions for the mobility. However, the overall structure of both integrals provide convenient ways of evaluating them. Equation 6 conforms with the case of generalized Hermite-Gauss quadrature, while eq 7 can be handled with the Laguerre-Gauss quadrature. In both cases the five point formulas were used⁸ for calculations in liquid xenon.

The maximal number of partial waves, l_{\max} , which is necessary to describe the scattering problem is given by

$$[l_{\max}(l_{\max} + 1)]^{1/2} \approx kA \quad (8)$$

l_{\max} in the present calculations did not exceed 16 (even though it caused enough troubles in calculating the higher-order spherical Bessel functions in (4)) and the infinite series in eq 5 could be truncated there.

Actual calculations were carried out in liquid argon and xenon, where all the necessary input parameters, with the only exception of A , were provided by experiments. A was determined by successive approximations. Its value was varied until the model gave a mobility equal to the experimental one.

3. Calculations in Liquid Xenon

For comparison we present our results for liquid xenon together with those obtained previously in liquid argon.⁷ Three sets of input data are needed for the calculations.

a. Thermodynamic data are needed which include the equation of state and the isothermal compressibility of the liquids. Because the mobility measurements are usually done along the vapor-liquid coexistence line, $(p, \langle n \rangle, T)$ and κ values are necessary along this line too, up to the critical point. Data for liquid argon are reported in ref 9 and for xenon in ref 10. Values for the isothermal

(8) F. B. Hildebrand: "Introduction to Numerical Analysis", McGraw-Hill, New York, 1956, p 325.

(9) W. B. Streett and L. A. K. Staveley, *J. Chem. Phys.*, **50**, 2302 (1969); A. L. Gosman, R. D. McCarty, and J. G. Hurst, *Nat. Stand. Ref. Data Ser. Natl. Bur. Stand.*, No. 27.

(10) W. B. Streett, L. S. Sangan, and L. A. K. Staveley, *J. Chem. Thermodyn.*, **5**, 633 (1973); F. Theeuwes, and R. J. Bearman, *ibid.*, **2**, 507 (1970).

(6) D. F. Calef and P. G. Wolynes, *J. Chem. Phys.*, **78**, 4145 (1983).
(7) A. Vertes, *J. Chem. Phys.*, **79**, 5558 (1983).

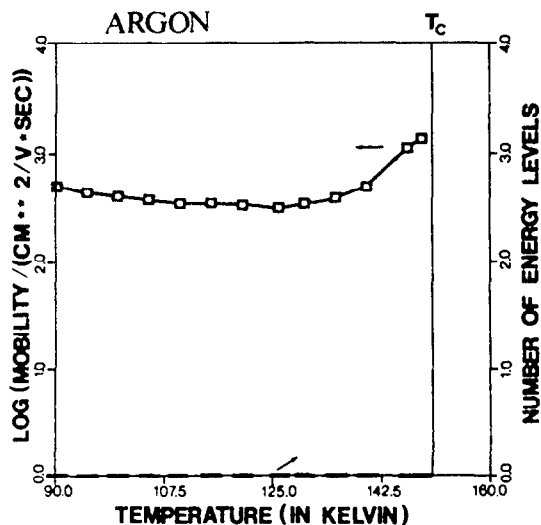


Figure 1. Logarithm of the electron mobility in liquid argon as a function of temperature (\square). Simultaneously, the number of possible energy levels in an average size fluctuation is displayed (—). There is no decrease in the mobility near the critical point and there is no increase in the number of energy levels either.

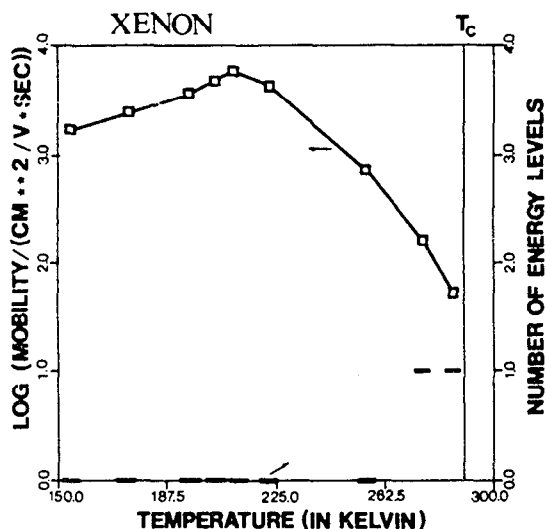


Figure 2. In liquid xenon, there is a dramatic drop in the mobility approaching the critical temperature (\square) and the number of energy levels in an average size fluctuation (—) goes up at the same time.

compressibility in liquid xenon closer to the critical point can be found in ref 11.

b. V_0 measurements must be as a function of density. For liquid argon Allen and Schmidt published the first density-dependent V_0 measurements.¹² Data for fluid xenon and krypton appeared about the same time from Reininger, Asaf, and Steinberger.¹³ Because of the experimental difficulties in V_0 measurements the published values usually contain 5×10^{-14} erg uncertainty which, in consequence, produces about 50% error in the derivative.

c. Zero field mobility measurements must be as a function of temperature and pressure. In fluid argon Jahnke, Meyer, and Rice¹⁴ made experiments over an extensive range of temperature and pressure under isobaric and isothermal conditions. Their measurements covered the vapor-liquid coexistence line under the critical point as well as its upward continuation. Huang and

TABLE I: Input Data Used for Mobility Calculations in Liquid Xenon

T, K	$\langle n \rangle, 10^{22} \text{ cm}^{-3}$	$\kappa, 10^{-11} \text{ cm}^2/\text{dyn}$	$\partial V_0/\partial n, 10^{-36} \text{ erg cm}^3$
154	1.40	13	140
174	1.32	19	140
195	1.25	27	125
204	1.22	32	110
210	1.20	36	100
222	1.15	48	30
255	0.99	143	-80
275	0.85	563	-110
286	0.67	2887	-120

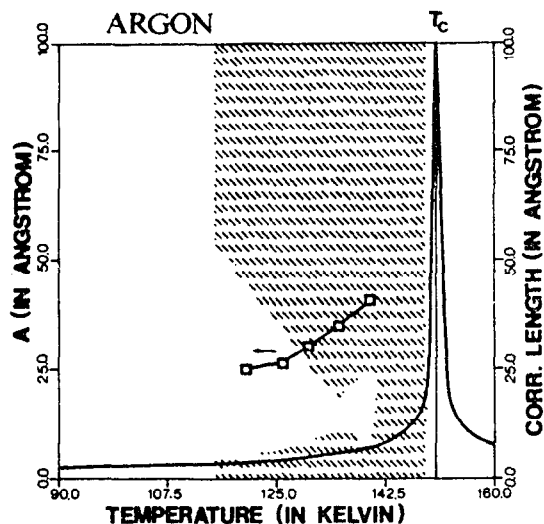


Figure 3. The average fluctuation size estimated from the present model in liquid argon (\square) as a function of temperature. The long-range correlation length, ξ , from eq 9 is also shown (solid line). The shaded region emphasizes where the Born approximation does not prevail. (Calculated on the basis of eq 1 and 2.)

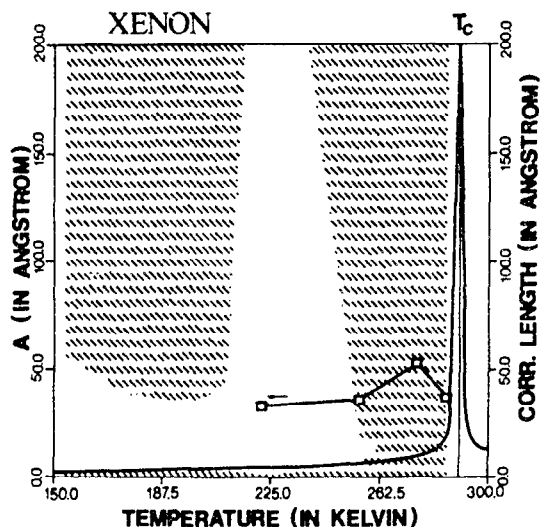


Figure 4. Average fluctuation size in liquid xenon as a function of temperature (\square) together with the long-range correlation length calculated from eq 9 (solid line). Our theory seems to break down in the vicinity of the critical point. The shaded regions represent the constraints produced by the Born approximation.

Freeman¹⁵ measured the mobility of excess electrons in liquid xenon along the vapor-liquid coexistence line.

The input data used for the calculations in liquid xenon are summarized in Table I. In Figure 1 the logarithm of electron

(11) J. Zollweg, G. Hawkins, and G. B. Benedek, *Phys. Rev. Lett.*, **27**, 1182 (1971).

(12) A. O. Allen and W. F. Schmidt, *Z. Naturforsch. A*, **37**, 316 (1982).

(13) R. Reininger, U. Asaf, and I. T. Steinberger, *Chem. Phys. Lett.*, **90**, 287 (1982).

(14) J. A. Jahnke, L. Meyer, and S. A. Rice, *Phys. Rev. A*, **3**, 734 (1971).

(15) S. S. S. Huang and G. R. Freeman, *J. Chem. Phys.*, **68**, 1355 (1978).

mobility in liquid argon is displayed as a function of temperature. Inspecting the curve makes it clear that no electron localization occurs even in the neighborhood of the critical point. In comparison in Figure 2 a different behavior can be observed for liquid xenon. The mobility of excess electrons drops two orders of magnitude toward the critical point.

The basic question is whether this decrease is due to an increasing localization of the electrons or if features inherent in the quasifree state can explain this dramatic change. As mentioned earlier the Born approximation is not applicable in the vicinity of the critical point. The constraints stated by eq 1 and 2 are represented in Figure 3 for argon and Figure 4 for xenon. The shaded domains show where the condition given in eq 1 or 2 is not fulfilled. It is clear that, relatively far from the critical point, the Born approximation in fact breaks down, independent of the (so far unknown) quantity A .

In the relevant temperature interval mobility calculations were carried out with the method of partial waves in both liquids. The parameter A was determined by successive approximations, matching the calculated mobility to the experimental one. In accordance with our expectations its value increases as the temperature approaches the critical temperature, T_c . This is reasonable if one takes into account the fact that the size of fluctuation diverges at the critical point. As a possible measure of fluctuation size one can take the long-range correlation length, ξ . This length is known to diverge at the critical point as

$$\xi = \xi_0 |1 - T/T_c|^{-\nu} \quad (9)$$

Light scattering experiments in liquid xenon gave $\xi_0 = 1.18 \pm 0.2 \text{ \AA}$ and $\nu = 0.57 \pm 0.05$ for the critical exponent.¹⁶ This function together with our previously determined A values are plotted in Figures 3 and 4. They show an overall similar trend except for the last point in the case of xenon.

The large discrepancy between the magnitude of A and ξ can mean one of two things. It either points out some deficiency of the theoretical treatment or appears as a consequence of the different objects the fluctuations scatter. In other words, one can say that A is different from ξ because A characterizes an average fluctuation size which scatters most of thermal electrons while ξ is obtained from light scattering.

A major deviation from the present theory appears at 286 K in xenon. At this point if the expected trend of the average fluctuation size was maintained, the theory would largely overestimate the electron mobility. This can mean one of two things. Either the whole present approach is meaningless in this region because of the linearity suppositions used in the solution of the Boltzmann equation and also involved in the fluctuation model or, if this is not the case, some new electronic state should be taken into account. The possibility of formation of localized states and the stability of electronic bubbles in liquid xenon will be examined in the Appendix.

4. Summary

Our primary goal was to extend the fluctuation model of quasifree electron mobility beyond the limitations of the Born approximation usually employed. First two independent satisfactory criteria were established for the applicability of the Born approximation. Examining the case of liquid argon and xenon shows that considerably below the critical temperature the Born approximation is already inappropriate.

The method of partial waves was introduced to overcome this difficulty. $\partial V_0/\partial n$, the usual fitting parameter, has been replaced by values derived from experimental $V_0(n)$ curves. Our model, however, introduces a new fitting parameter, A , the average size of fluctuations or, in another interpretation, the influence range of the scattering potential. This parameter was determined by successive approximations to give agreement between the measured and calculated mobility. A as a function of temperature shows a similar shape to the long-range correlation length; however, its value is much larger.

The only deviation from the expected monotonic trend in the average fluctuation size can be observed in liquid xenon very near to the critical temperature. This discrepancy is either due to the failure of linearized relationships invoked at several points of the theory or a consequence of electron localization.

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Appendix. The First Step of Electron Localization in Nonpolar Liquids

The overall thermodynamics of electron localization in nonpolar liquids was investigated by Springett, Jortner, and Cohen.⁴ They established a stability criterion for the localized state in terms of the formation of a so-called electronic bubble. Their theory predicts whether a relaxed localized state can exist at all; however, nothing is said about the manner and possibility of their formation.

On the basis of picosecond electron transfer experiments⁵ the localization of quasifree electrons is thought to consist of two consecutive steps. The first step is a temporary localization of an electron in a shallow trap formed by a fluctuation in the liquid, while the second one is the relaxation of the molecules around the electron resulting in a deepening of the trap.

The most recent description of the second step was given by Calef and Wolynes.⁶ They treated the relaxation process by considering the structured nature of the liquid during the charge solvation. Use was made of the Schmoluchowski-Vlasov equation to find the time dependence of the trap depth around an electron. Their results can be brought into good accordance with the sporadic experimental findings in this field.

No attempt has been made so far to the best of our knowledge to deal with the first step, i.e., with electron localization in a shallow trap formed by a fluctuation. In the following we propose a simple semiquantitative treatment for a necessary condition in shallow trap formation.

If we made use of the basic thermodynamic relationship for density fluctuations

$$\frac{\langle \Delta n^2 \rangle}{\langle n \rangle^2} = \frac{3k_B T \kappa}{4A^3 \pi} \quad (10)$$

and eq 3 for the resulting potential, the average trap depth in the absence of electrons can be expressed in the following way:

$$\langle \Delta V_0 \rangle = \frac{1}{2} (3k_B T \kappa / A^3 \pi)^{1/2} \frac{\partial V_0}{\partial n} \langle n \rangle \quad (11)$$

The number of $l = 0$ energy levels, N_e , in a spherical potential well can be expressed by¹⁷

$$N_e = \text{INT} [\rho / \pi + 1/2] \quad (12)$$

where $\rho = (2m\Delta V_0)^{1/2} A / \hbar$ and INT denotes the integer part function. The detailed form of ρ

$$\rho = (3k_B T / \pi)^{1/4} (|\partial V_0 / \partial n| \langle n \rangle m_e)^{1/2} \kappa^{1/4} A^{1/4} / \hbar \quad (13)$$

shows that the number of the available energy levels in the vicinity of the critical point will diverge as $(\kappa A)^{1/4}$.

Using ξ instead of A we evaluated eq 12 for liquid argon and xenon. The results are displayed in Figures 1 and 2. It is remarkable that in argon even in the neighborhood of the critical temperature there is no available $l = 0$ energy level in an average fluctuation. This may be the reason for the conservation of the quasifree state throughout the whole investigated temperature range. In liquid xenon, however, already at $T = 275.2 \text{ K}$ an energy level appears in the average fluctuation promoting the formation of the localized state. As we have seen before at $T = 275.2 \text{ K}$

the mobility can be explained with the quasifree state alone but at $T = 285.8$ K localization should be considered.

Electronic bubble stability calculations in liquid xenon show that there are no stable bubbles in the system below 275.2 K and stable bubbles exist at higher temperatures. The bubble radii at 275.2 and 285.8 K are 5.3 and 6.6 Å, respectively. There is an interesting coincidence between the appearance of stable bubbles at 275.2 K and the formation of energy levels in V_0 fluctuations. This is of course only an accidental agreement since the theory

in ref 4 establishes the equilibrium criteria for the existence of electronic bubbles while our contribution concerns the first step of their formation kinetic.

A detailed description of the first stage of electron localization should provide the transition probabilities between the quasifree and localized states as well as an understanding of the energy transfer during the process.

Registry No. Xenon, 7440-63-3.

Deuterated Liquid Ammonia and ${}^7\text{Li}\cdot 4\text{ND}_3$ Solution. A Neutron Scattering Investigation

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One presents the structure factor and the radial distribution function of liquid ammonia at +22 and -65 °C as obtained from neutron diffraction measurements. The same results are given for a ${}^7\text{Li}\cdot 4\text{ND}_3$ solution at -57 °C. These data are compared and discussed. The effect of dilution on the structure of the lithium solution is also shown. There is definite evidence for an ordering due to the solvated lithium ion.

Considerable progress has been made in recent years in the determination of the structure of molecular liquids. In particular, the combination of X-ray scattering and neutron scattering on isotopically substituted samples has enabled us to precisely determine the intramolecular parameters in the liquid state and the distribution of the intermolecular positions and to obtain some information on the angular correlation functions.¹ We shall in this paper present and discuss some results of a neutron scattering research program devoted to liquid ammonia as well as to concentrated metal-ammonia solutions.² A detailed analysis of these experiments became recently possible due to the progress³ in the correction of the strong inelasticity effect presented by light atom containing molecules. This work, which does not, for the time being, take full advantage of the isotopic substitution technique⁴ (such as would be possible for ${}^{14}\text{N}/{}^{15}\text{N}$, H/D, or ${}^6\text{Li}/{}^7\text{Li}$, etc.), provides, however, some insight on the local order of these systems. After a few words on the experimental aspects, we shall focus successively on the intramolecular parameters, the intermolecular ordering, and the hydrogen bonding of pure liquid ammonia and then compare it to the ${}^7\text{Li}\cdot 4\text{ND}_3$ solution where the effects of the solvation shell will be emphasized.

Experimental Section

A very large series of experiments has been performed on pure liquid ND_3 (as well as on a ${}^7\text{Li}(\text{ND}_3)_4$ solution) in order to check

the incident neutron energy effect on the inelasticity correction ($\lambda = 10, 2.53, 0.7, 0.5$, and 0.35 Å (at the I.L.L.), 1.33 Å (at Saclay), and down to 0.2 Å (on the Harwell Linac machine)). Various container materials such as vanadium or quartz and sample cell diameters from 7 to 15 mm have also been investigated. We shall, however, not report here on studies related to various technical aspects of the data analysis or to detailed comparisons between different neutron scattering machines and sample environments.²

The present paper refers only to experiments performed on the D4 liquid spectrometer, at the I.L.L. (Grenoble), at wavelengths $\lambda = 0.696$ Å (Zn 002) and $\lambda = 0.504$ Å (Cu 220), with filtering of the $\lambda/2$ neutrons. The data were collected every 0.2° (2 θ) step, with a single ${}^3\text{He}$ detector (10 cm long, 5-bar ${}^3\text{He}$ pressure) at a sample-to-detector distance of 1.50 m. The setting corresponds to a resolution of $\Delta Q/Q \approx 0.04$ at a scattering angle equal to the monochromator takeoff angle of 16° . The counting time was such as to obtain a statistical accuracy of 1% or better. The room temperature ammonia sample (99.75% enriched ND_3 (CEA, Saclay, France)), was contained in a 15-mm-diameter, 0.15-mm-thick vanadium container. The ${}^7\text{Li}$ -ammonia sample (${}^7\text{Li}$ from Oak Ridge) prepared in Prof. Lepoutre's laboratory (Lille) with a 19.4 MPM composition, determined by gravimetry of the lithium and gas volumetry of the ammonia, was contained in a 8-mm-i.d., 10-mm-o.d. sealed quartz cell. An identical quartz cell was used for the low-temperature ammonia experiment and for the other lithium-ammonia concentrations. In all cases, the sample height illuminated by the neutron beam was 5 cm.

The low-temperature ammonia sample and the Li-ammonia solutions were refrigerated at the top and bottom ends by two copper blocks maintained at a regulated temperature (± 0.2 °C), the cold source being ensured by a solid connection to a liquid nitrogen bath. Thermal gradients along the sample were reduced by an aluminum heat shield of a large diameter (47 cm) with openings for the incoming and scattered neutron beam. They were estimated to 2–3° at most. The temperature was read from a platinum thermometer placed near the sample.

In all experiments the sample environment (such as a 50-cm-diameter vacuum vessel around the sample) was designed to

(1) (a) H. Bertagnolli, P. Chieux, and M. D. Zeidler, *Mol. Phys.*, **32**, 759 (1976). (b) H. Bertagnolli and M. D. Zeidler, *ibid.*, **35**, 177 (1978). (c) H. Bertagnolli, D. O. Leicht, M. D. Zeidler, and P. Chieux, *ibid.*, **36**, 1769 (1978). (d) H. Bertagnolli and P. Chieux, *Mol. Phys.*, submitted for publication.

(2) A report on the more technical aspects of the various corrections tested on this system shall be published, as well as data on different metal-ammonia solutions.

(3) See for example (a) J. G. Powles, *Adv. Phys.*, **22**, 1 (1973); (b) J. G. Powles, *Mol. Phys.*, **32**, 301, 323 (1976); **36**, 1161 (1978); (c) J. R. D. Copley, "Physics of Modern Materials", IAEA, Vienna, 1980, p 613; (d) H. Bertagnolli and P. Chieux, *Mol. Phys.*, submitted for publication.

(4) See for example (a) G. W. Neilson and J. E. Enderby, *Proc. R. Soc. London Ser. A* **390**, 353–71 (1983); (b) A. H. Narten, W. E. Thiessen, and L. Blum, *Science*, **217**, 1033 (1982); (c) see also ref 1.