MEASUREMENT OF THE DIELECTRIC CONSTANT OF LIQUID DEUTERIUM AND DEUTEROHYDROGEN

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The dielectric constants of liquid deuterium and deuterohydrogen have been measured by the resonance technique at frequencies $\sim 10^{10}$ Hz along the liquid-vapor equilibrium curve from the triple-points of the substances investigated down to 20.4°K. The Clausius-Mossotti functions for normal deuterium and deuterohydrogen are calculated. The mean values are respectively $(0.499 \pm 4 \times 10^{-4})$ cm^3/g and $(0.6694 \pm 5 \times 10^{-4})$ cm^3/g. The polarizabilities of molecules of hydrogen isotopes are compared: $\Delta\alpha_{H_2-HD} / \alpha_{n-H_2} = 0.65\%$ and $\Delta\alpha_{H_2-n-D_2} / \alpha_{n-H_2} = 1.35\%$.

IN this work we have measured the dielectric constants of liquid normal deuterium, liquid equilibrium deuterium and liquid deuterohydrogen at T = 20.4°K.[1] The experimental substances were under saturation vapor pressure at temperatures from their triple points to 20.4°K. The measurements were carried out by the resonance method at microwave frequencies ($\lambda \sim$ 3 cm). The dielectric constant was calculated from the formula

$$\varepsilon = (f_0 / f)^2, \qquad (1)$$

where f_0 and f are respectively the resonance frequencies when the measuring resonator is empty and filled with the substance.[2] The temperature was measured by a hydrogen condensation thermometer; data on the saturation vapor pressure of hydrogen given in[3] were used.

In the preparation of deuterium and hydrogen with equilibrium ortho-para composition at low temperatures, the conversion in the liquid was accelerated by means of the effective catalysts $Cr(OH)_3$ or $Fe(OH)_3$[4]. Since the measuring part of the setup was intended for work with ortho- and para-modifications and mixtures of the two, the catalyst was situated in a separate ampoule at T = 20.4°K from which the substance was recondensed into the resonator or the thermometer.

In order to obtain a sample of normal deuterium, we used factory n—D_2 with a certified isotopic impurity content <0.5%. The original deuterohydrogen was obtained by decomposition of lithium hydride by heavy water. The procedure differed somewhat from that described in[5,6]; the heavy water was frozen, pulverized LiH was then poured on to it and the substances were warmed to 0°C. This resulted in the reaction

$$LiH + D_2O \rightleftarrows LiOD + HD.$$

The high isotopic purity of the samples of D_2 and HD was ensured by distillation of the original mixtures in a four-stage unpacked fractionating column. The amount of isotopic impurities in the D_2 and HD was estimated,
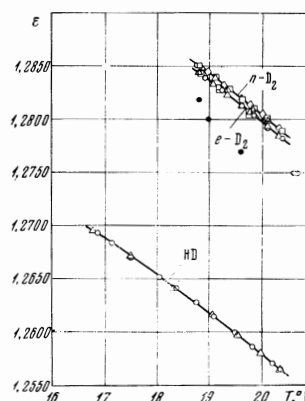
●—n-D_2 measurements of Itterbeek and Spaepen [1]. The precision of the measurement of the dielectric constant in [1] is ±5 × 10⁻⁴. The other symbols refer to different cycles of measurements in the present work. The curves $\epsilon(T)$ for n-D_2 and e-D_2 are shifted relative to each other by $\Delta\epsilon = 6.3 \times 10^{-4}$.

taking account of the column parameters and distillation rate parameters and was less than 0.05%. The mean error in the measurement of the dielectric constant was $\pm 5 \times 10^{-5}$.

Several cycles of measurements were performed, the results of which fall, within the above error-limits, on the same experimental curve (see the Figure) for each isotope.

In Tables I—III we give values of the dielectric constants of n—D_2, e—D_2 and HD, data on the density (ρ) of n—D_2[7] and HD[3] at the corresponding temperatures, and also values of the Clausius-Mossotti (C–M) function

$$P = \frac{\varepsilon - 1}{\varepsilon + 2} \frac{1}{\rho}.$$

The magnitude of P for equilibrium deuterium has not been calculated because of the lack of data on the density of e—D_2.

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[1] The dielectric constant of liquid n-D_2 has been investigated before [1]. There are no published data on the measurement of ϵ for liquid deuterohydrogen or liquid equilibrium deuterium at 20°K.

Table I

n-D$_2$, 66.67% orthomolecules							
First cycle of measurements				Second cycle of measurements			
T, °K	ϵ	ρ, g/cm^3	P, cm^3/g	T, °K	ϵ	ρ, g/cm^3	P, cm^3/g
20.39	1.27878	0.17042	0.4989	20.31	1.27915	0.1706	0.4990
20.14	1.2799	0.17092	0.4993	19.99	1.28039	0.1713	0.4989
19.85	1.2810	0.17162	0.4990	19.76	1.2813	0.17182	0.4989
19.56	1.28214	0.17224	0.4991	19.26	1.2832	0.17286	0.4990
19.25	1.2832	0.17288	0.4989	18.95	1.28446	0.1735	0.4992
18.76	1.28506	0.1739	0.4990	18.83	1.2849	0.17375	0.4992

Table II

e-D$_2$, 97.8% orthomolecules		e-D$_2$, 97.8% orthomolecules	
T°, K	ϵ	T°, K	ϵ
First cycle		Second cycle	
20.37	1.2783	20.345	1.27842
20.09	1.27938	20.106	1.2794
19.83	1.28046	19.86	1.28038
19.62	1.28135	19.49	1.2819
19.23	1.28282	18.92	1.2839
18.91	1.28392		

Table III

HD				HD			
T°, K	ϵ	ρ, g/cm^3	P, cm^3/g	T°, K	ϵ	ρ, g/cm^3	P, cm^3/g
20.35	1.25653	0.11759	0.6699	18.36	1.26413	0.12092	0.6692
20.205	1.25714	0.11785	0.6699	18.045	1.26523	0.12139	0.66915
19.82	1.25863	0.11853	0.6696	17.49	1.26715	0.1222	0.66914
19.49	1.25994	0.1191	0.6695	17.13	1.2684	0.1227	0.6693
19.08	1.26144	0.11976	0.6694	16.76	1.26959	0.12321	0.6692
18.75	1.2628	0.12029	0.6696				

Table IV

α_{n-H_2}, A^3	α_{HD}, A^3	α_{n-D_2}, A^3	$\dfrac{\alpha_{n-H_2} - \alpha_{HD}}{\alpha_{n-H_2}}$, %	$\dfrac{\alpha_{n-H_2} - \alpha_{n-D_2}}{\alpha_{n-H_2}}$, %	Source
0.779	—	0.769	—	1.3	[10]
0.789	—	0.787	—	0.25	[1]
0.7894	0.7829	0.7749	0.82	1.84	[13]
—	—	—	0.56	1.26	[14]
0.8076	0.8023	0.7967	0.65	1.35	[9] and the present work

The range of densities at which measurements of the dielectric constant were carried out is small, especially for D$_2$. It is probably for this reason that the C-M function for deuterium does not display any change, and is equal to (0.499 ± 4 × 10^{-4}) cm^3/g. In the case of HD a tendency appears towards increase of P with decrease in the density, ΔP = 5 × 10^{-4}; this does not exceed the experimental error (for $\Delta\rho/\rho$ = 0.05%). The average magnitude is P$_{HD}$ = (0.6694 ± 5 × 10^{-4}) cm^3/g. We should note that on using the density data from[8], an "anomalous" change is observed in the magnitude of P$_{HD}$ (~0.3%) and in the sign (P increases with increase in the density).

From the values of the C-M function at 20.4°K for n—D$_2$ and HD (the present work) and n—H$_2$[9], the difference in the polarizabilities of molecules of the hydrogen isotopes has been estimated (see Table IV).

In Table IV the results of a number of experimental investigations in which the polarizabilities of H$_2$, HD, and D$_2$ were determined are brought together. These investigations differ in their methods and experimental conditions: 1) in[1] the dielectric constants of liquid n—D$_2$ and n—H$_2$ at temperatures below 22°K were measured by a beat method at frequencies ~530 kHz; 2) in[10] α_{n-H_2} and α_{n-D_2} are compared at zero frequency from measurements of the refractive index and dispersion in gaseous D$_2$ and H$_2$ at room temperature[11-13]; 3) in[14] the isotopic effect in the polarizabilities was measured by a comparative method with a capacitance bridge for gaseous H$_2$, HD and D$_2$ at T = 77.3°K. The C—M equation was used in these papers to determine α.

A theoretical calculation of the polarizabilities of H$_2$, HD and D$_2$ molecules is given in[15].

From Table IV it can be seen that the experimental values at present available for the relative differences in the polarizabilities of molecules of the hydrogen isotopes, obtained from measurements of the dielectric characteristics (the present paper and[10,14]), are evidence that $\Delta\alpha/\alpha$ has no temperature dependence in the interval 20—300°K.

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PSEUDOMULTIPLICITY UNCERTAINTY IN SUPERCONDUCTIVITY THEORY

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We consider the uncertainty in the population and the ensuring uncertainty of the pseudospin projections in a system described by a Bardeen-Cooper-Schrieffer (BCS) Hamiltonian. We show that the uncertainty of the population and of the energy gap associated with it is independent of the anomalous mean values. A method, based on allowance for the uncertainty of the total pseudospin with conservation of the total number of electrons in the system is considered. An exact solution is given for the case of one Cooper pair and two phase-space cells; this solution leads to an energy that does not depend on the sign of the parameter of the interelectron interaction and lies below the energy of the ground state calculated by the BCS method. It is shown that L. Cooper's problem admits of the existence of a gap between the ground state of the system and the continuum not only in the case of attraction but also in the case of sufficiently strong interelectron repulsion. Modifications of the trial wave function, which make it possible to include in the BCS method the case of interelectron repulsion, are considered. The role of large or small pseudospins is assessed in the case of interelectron attraction or repulsion.

1. INTRODUCTION

THE BCS method[1], the importance of which to the development of superconductivity theory is well known, is equivalent to the pseudomagnetic field approximation[2]. This method is connected with introduction of fictitious states and takes into account the possibility of superconductivity only in the case of interelectron attraction. Yet it is known from quantum theory of magnetism that a corresponding magnetic order can be obtained for any sign of the spin-interaction parameter. This gives grounds for expecting that in the case of the interelectron interaction described in the BCS theory by the parameter V, the corresponding ordering can occur at any sign of this parameter[1]. We show in this article that the expected analogy between magnetism and superconductivity can indeed be established.

2. POPULATION UNCERTAINTY IN THE BCS THEORY

The BCS theory[1] starts from the Hamiltonian

$$H = \sum_{\sigma,\, k > k_F} \varepsilon_k n_{k\sigma} + \sum_{\sigma,\, k < k_F} |\varepsilon_k|(1 - n_{k\sigma}) - \sum_{k,\, k'} V_{kk'} b_k^* b_k, \quad (1)$$

where σ, k, and ϵ_k are the spin projection, wave vector, and kinetic energy of the conduction electron; k_F is the Fermi wave vector; $n_{k\sigma}$ is the operator of the number of electrons in the state (k, σ); b_k^* is the Cooper pair production operator; $V_{kk'}$ is the matrix element, assumed equal to zero when $|\epsilon_k| > \hbar\omega$ and equal to a constant V when $|\epsilon_k| < \hbar\omega$, where ω is the average phonon frequency. The approximation used in[1] for the ground-state wave function is

$$\Psi = \prod_k [(1 - h_k)^{1/2} + h_k^{1/2} b_k^*]\Phi_0, \quad (2)$$

where h_k is the probability that the pair fills the state $(k, \sigma; -k, -\sigma)$, and Φ_0 is the vacuum wave function.

In the approximation (2), the mean value of the Hamiltonian (1) is

$$W = \sum_k |\varepsilon_k|(1 - \sqrt{1 - 4(\bar{b}_k)^2}) - V \sum_{k,\, k'} \bar{b}_{k'} \bar{b}_k. \quad (3)$$

This expression has a minimum with respect to b_k if the following equality is satisfied:

$$\bar{b}_k = \varepsilon_0 [2\sqrt{\varepsilon_k^2 + \varepsilon_0^2}]^{-1}, \quad \varepsilon_0 = V \sum_{k'} \bar{b}_{k'}. \quad (4)$$

From (3) and (4) follow the known results of the BCS theory[1]:

$$\varepsilon_\bullet = \hbar\omega \left[\operatorname{sh}\left(\frac{1}{N_0 V} \right) \right]^{-1}, \quad W_0 = -2N_0(\hbar\omega)^2 [e^{2/N_0 V} - 1]^{-1},$$

where N_0 is the density of states at the Fermi surface.

It is easy to verify that the BCS variational problem was solved relative to the uncertainty of the population of the phase space, which is determined by the expression

$$\Delta n_{k\sigma} = \overline{((n_{k\sigma} - \bar{n}_{k\sigma})^2)}^{1/2} = [\bar{n}_{k\sigma}(1 - \bar{n}_{k\sigma})]^{1/2} = \bar{b}_k, \quad (5)$$

where it is recognized that $n_{k\sigma}^2 = n_{k\sigma}$ for Fermi particles and that according to (2) $\bar{b}_k = \sqrt{h_k(1 - h_k)}$. It follows from (5) that in the BCS method the difference between $\Delta n_{k\sigma}$ and zero is due to the inequality

$$\bar{b}_k \neq 0, \quad (6)$$

which follows from (4) and is usually regarded as the "gist of the BCS theory"[5]. We shall show that actually expression (5) does not hold, and that the existence of the uncertainty $\Delta n_{k\sigma}$ is not connected with satisfaction of (6).

The operators b_k and $N_\sigma = \sum_k n_{k\sigma}$ satisfy the commutation relation

$$b_k N_\sigma - N_\sigma b_k = b_k. \quad (7)$$

On the other hand, the operator N_σ commutes with the Hamiltonian (1). It follows therefore from (7) that in the stationary state, in which N_σ has a negative value,

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[1]The need for developing a method different from that of [1] in order to take into account both signs of V is noted in [3,4].