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Nuclear quadrupole spin-lattice relaxation mechanism due to reorientation of the molecular fragments between unequal potential wells in a crystal

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A comparative analysis is made of the effectiveness of the magnetic and quadrupole modulation mechanisms of spin-lattice relaxation for quadrupole nuclei following reorientation of a neighboring molecular fragment that moves between equilibrium positions separated by unequal potential barriers. The results of the analysis are used to interpret the experimental data obtained for $T_1(T)$ in a $CL_3P=NCCl(CF_3)_2$ crystal by the method of nuclear quadrupole resonance on the chlorine nuclei of a $CCl(CF_3)_2$ fragment moving in a potential with unequal wells and of the PCl_3 group that is nonvalently bound to this fragment.

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The reorientation motion of atom groups in a crystal can act on the relaxation of neighboring nuclei by modulating either the magnetic or the electric interactions. For reorientations in an "equal-well" potential, it was shown in a number of cases[1-4] that modulation of the electric quadrupole interaction with the moving neighbors leads to a more effective relaxation mechanism for nuclei with large quadrupole interactions (halogens in covalent bonds, in contrast, e.g., to nitrogen nuclei[5]). The purpose of the present paper is to elucidate the distinguishing features of various modulation mechanisms and their effectiveness in reorientation motion of atomic groups between unequal potential wells. The modulation due to "unequal-well" motion was observed by us experimentally in the crystal $Cl_3P=NCCl(CF_3)_2$. In this compound one observes the influence of reorientational motion of the asymmetrical fragment $CCl(CF_3)_2$ between three equilibrium positions separated by unequal potential barriers, on the spin-lattice relaxation of the chlorine nuclei in the PCl_3 group.[6] Therefore in the exposition that follows all the concrete numerical estimates that follow from the theoretical analysis are made by us for chlorine nuclei (spin 3/2) and are valid for a large class of chlorine-containing compounds.

1. MODULATION OF MAGNETIC DIPOLE-DIPOLE INTERACTONS

Let a nucleus with spin I and nonzero electric quadrupole moment be coupled to n neighboring magnetic nuclei having a spin S and a magnetic dipole-dipole interaction described by the Hamiltonian

$$\mathscr{H}_{dd}=\gamma_I\gamma_S\hbar^2\sum_i^n\frac{(\mathbf{IS}_i)r_i^2-3(\mathbf{Ir}_i)(\mathbf{S}_i\mathbf{r}_i)}{r_i^5}=f(r_i,\theta_i,\varphi_i). \tag{1}$$

Here r_i, θ_i, φ_i are the polar coordinates of the radius vector $\mathbf{r}_i$ joining the quadrupole nucleus with the ith magnetic nucleus in the system of the principal axes of the tensor of the electric field gradient (EFG) at the quadrupole nucleus. If the cause of the nuclear spin-lattice relaxation are random modulations of this interaction, which result from the reorientational molecular motions, then the probability of the relaxation transition between states m and m' for a quadrupole nucleus with $I=3/2$ is given by[7]

$$W_{mm'}=\hbar^2\int_{-\infty}^{\infty}g_{mm'}(\tau)\exp(-i\omega_Q\tau)\,d\tau, \tag{2}$$

where $g_{mm'}=\mathrm{Sp}\,\mathscr{H}_{mm'}(0)\mathscr{H}_{m'm}(\tau)$ is the correlation function (the summation under the spur sign is carried out over all the states of the magnetic nuclei), $\omega_q=2\pi v_Q$, v_Q is the frequency of the nuclear quadrupole resonance (NQR) of the considered nucleus.

In analogy with Ref. 5 we can obtain for the probabilities W and W of one-quantum and two-quantum transitions, respectively, in the general case of arbitrary EFG symmetry, the expressions

$$W_1=\frac{9}{32}\left(1+\frac{2}{1+\eta^2/3}\right)\frac{(\gamma_I\gamma_S\hbar)^2}{\omega_Q}\sum_i\frac{1-\cos^4\theta_i}{r_i^6}F, \tag{3}$$

$$W_2=\frac{9}{4}\left(1-\frac{1}{1+\eta^2/3}\right)\frac{(\gamma_I\gamma_S\hbar)^2}{\omega_Q}\sum_i\frac{\sin^2\theta_i\cos^2\theta_i}{r_i^6}F, \tag{4}$$

where η is the asymmetry parameter of the EFG tensor, F is a function of the dimensionless parameter $\omega_Q\tau_c$,

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τ_c is the correlation time of the motion in which the magnetic nuclei take part. The spin-lattice relaxation time for nuclei with spin 3/2 is given by

$$T_1^{-1}=2(W_1+W_2). \tag{5}$$

Depending on the form of the molecular motion, we can consider several concrete situations.

a) In the simplest case of reorientational motion of magnetic nuclei between several equilibrium positions separated by equal potential wells,[5]

$$F=2\omega_Q\tau_c/(1+\omega_Q^2\tau_c^2). \tag{6}$$

b) When the magnetic nuclei jump over between two equilibrium positions A and B characterized by potential wells of unequal depth ($E_A-E_B\equiv\Delta$, where E_A and E_B are the corresponding potential barriers),[8]

$$F=\frac{4P_AP_B}{(P_A+P_B)^2}\frac{2\omega_Q\tau_c}{1+\omega_Q^2\tau_c^2}. \tag{7}$$

Here P_A and P_B are the stationary probabilities that the reorienting group of atoms will stay in the positions A and B (here $P_A/P_B=e^{\Delta/RT}$), $\tau_c^{-1}=\tau_{cA}^{-1}+\tau_{cB}^{-1}$ (τ_{cA}^{-1} and τ_{cB}^{-1} are the probabilities of jumps from positions A and B).

c) In the case of reorientational motion between three positions, two of which correspond to potential wells of equal depth [position (B)] while the third (A) corresponds to a well deeper by an amount Δ, the separating barriers having only two values, E and $E+\Delta$ (two-parameter model of three-well potential[9]),

$$F=9P_AP_B\frac{\omega_Q\tau_{c1}}{1+\omega_Q^2\tau_{c1}^2}+3P_B\frac{\omega_Q\tau_{c2}}{1+\omega_Q^2\tau_{c2}^2}, \tag{8}$$

where

$$\begin{gathered}P_A=[1+2\exp(-\Delta/RT)]^{-1},\quad P_B=\exp(-\Delta/RT)[1+2\exp(-\Delta/RT)]^{-1},\\ \tau_{c1}=\tau_0[1+2\exp(-\Delta/RT)]^{-1}\exp(E/RT),\quad \tau_{c2}={}^1/_3\tau_0\exp(E/RT).\end{gathered} \tag{9}$$

To determine the contribution of the considered mechanism to the relaxation rate it is necessary to carry out a comparative estimate of the quantities in (3) and (4). It can be shown first that in our case (chlorine nuclei) the probability of one-quantum relaxation transitions is much higher than the probability of two-quantum transitions, (i.e., $W_1\gg W_2$). At all values of the asymmetry parameter of the EFG tensor ($0\leqslant\eta\leqslant 1$) the ratio

$$\left(1+\frac{2}{1+\eta^2/3}\right)\Big/\left(1-\frac{1}{1+\eta^2/3}\right)$$

ranges from infinity to 10. For the usual values (in the case of monovalent chlorine atoms) $\eta\approx 0.1$ this ratio is $\sim 10^3$. In addition, it can be easily verified that the trigonometric functions of the angles θ, which are not equal to zero in (3), are always larger than in (4). Thus, in this case the magnetic modulation mechanism can lead to a substantial contribution to T_1^{-1} only on account of one-quantum transition.

A numerical estimate of the coefficient of F in expression (3) for W_1 in the case of dipole-dipole interactions of magnetic (e.g., ^{1}H, ^{19}F) and quadrupole (^{35}Cl) nuclei leads to relatively small values of this coefficient (cf. the estimates in Sec. 2). Thus, at $\theta\sim 30°-90°$ and at r not less than 1–2 Å it is of the order of (10^1-10^{-1}) sec.

To continue the estimate we must analyze the functions F in the three mentioned situations. In case (a), the maximum value $F_{\max}=1$ is obtained at $\omega_Q\tau_c=1$. Both for $\omega_Q\tau_c\ll 1$ (high-temperature limit) and for $\omega_Q\tau_c\gg 1$ (low temperature limit) we have $F\ll 1$. In cases (b) and (c), when the equilibrium position is characterized by different potential barriers ($\Delta>0$), the maximum of the function F decreases. At large Δ ($\Delta\gg RT$) we have $F_{\max}=4e^{-\Delta/RT}$ in case (b) and $F_{\max}=5.5e^{-\Delta/RT}$ in case (c).

Thus, for the considered mechanism of relaxation of quadrupole nuclei when the magnetic neighbors move in an equal-well potential (case a) the values of $W_{1\max}$ lie in the range 10^1-10^{-1} sec^{-1}. If the motion is between substantially unequal wells (cases b and c) the values of $W_{1\max}$ would be only $10^{-1}-10^{-3}$ sec^{-1} even at $\Delta/RT\approx 5$. In thiscase $T_{1\max}$ would be of the order of 10^1-10^3 sec, much higher than the customarily observed values. Consequently the contribution of the magnetic modulation mechanism to the relaxation of quadrupole nuclei is negligibly small in this case compared with the libration mechanism due to fluctuations of the mean squared amplitudes of the rotational swings of the molecules.[10]

2. MODULATION OF THE ELECTRIC FIELD GRADIENT AT A QUADRUPOLE NUCLEUS

The relaxation mechanism connected with modulation of quadrupole interactions of a resonant nucleus, and first considered for equal-well motion by Woessner and Gutowsky,[11] presupposes fluctuations of that small part of the EFG which is produced by a moving atomic group in the neighborhood of the quadrupole atom. If we regard as a perturbation that nonsecular part of the Hamiltonian $\mathscr{H}(t)$ which is connected with the indicated fraction of the EFG (relative to the principal Hamiltonian $\mathscr{H}_0$), then in the case of nuclei with spin 3/2 we can obtain the following expression for the transition probabilities[11]:

$$\begin{aligned}W_1&=\frac{1}{12}\frac{e^2Q^2}{\hbar^2}\int_{-\infty}^{\infty}\mathrm{Re}\langle q_{\mp1}(t)q_{\mp1}^*(t+\tau)\rangle\exp(-i\omega_Q\tau)\,d\tau,\\ W_2&=\frac{1}{48}\frac{e^2Q^2}{\hbar^2}\int_{-\infty}^{\infty}\mathrm{Re}\langle q_{\mp2}(t)q_{\mp2}^*(t+\tau)\rangle\exp(-i\omega_Q\tau)\,d\tau,\end{aligned} \tag{10}$$

where $q_{\mp1}$ and $q_{\mp2}$ are the transition-inducing components of the EFG tensor, due to the perturbation, at the nucleus with the quadrupole moment Q. The real parts of the correlation functions, say in the case of motion between potential wells A and B of unequal depth (case b of the preceding section) can be represented in the form

$$\begin{aligned}\mathrm{Re}\langle q_{\mp1}(0)q_{\mp1}^*(\tau)\rangle&\approx a_1+b_1\frac{2P_AP_B}{(P_A+P_B)^2}\exp(-\tau/\tau_c),\\ \mathrm{Re}\langle q_{\mp2}(0)q_{\mp2}^*(\tau)\rangle&\approx a_2+b_2\frac{2P_AP_B}{(P_A+P_B)^2}\exp(-\tau/\tau_c),\end{aligned} \tag{11}$$

where $a_{1,2}$ and $b_{1,2}$ are certain constants that depend on the polar coordinates of the moving nuclei (in the reference frame of the EFG tensor axes). Using expressions (5), (10), and (11) we obtain

$$T_1^{-1}=\frac{1}{12}\frac{e^2Q^2}{\hbar^2}(4b_1+b_2)\frac{4e^\alpha}{(1+e^\alpha)^2}\frac{\tau_c}{1+\omega_Q^2\tau_c^2}, \tag{12}$$

where $\alpha\equiv\Delta/RT$, $\tau_c^{-1}=\tau_{cA}^{-1}+\tau_{cB}^{-1}$.

In the particular case of wells of equal depth ($\Delta=0$) expression (12) goes over into the Woessner-Gutowsky equation[11]:

$$T_1^{-1}=\frac{1}{12}\frac{e^2Q^2}{\hbar^2}(4b_1+b_2)\frac{\tau_c}{1+\omega_Q^2\tau_c^2},\tag{13}$$

where $b_i=\langle|q_{\pm i}(0)|^2\rangle$.

If we introduce the notation $4b_1+b_2=(q')^2$, where q' stands for the fraction of the EFG produced at the quadrupole nucleus by the moving group, then, since $\hbar\omega_Q=eQq/2$ (q is the z-component of the total axisymmetric EFG tensor at the quadrupole nucleus), expression (12) reduces to

$$T_1^{-1}=\frac{1}{12}\frac{(eQq')^2}{\omega_Q\hbar^2}F,\tag{14}$$

or

$$T_1^{-1}=\frac{1}{3}\omega_Q(q'/q)^2F.\tag{15}$$

It is important that the function F is the same as in the preceding section [relations (6)–(8)], so that all the conclusions concerning its dependence on the degree of inequality of the potential-well depths remain in force here too. Consequently, the analysis of the possible contribution of the considered mechanism to the relaxation of the quadrupole nuclei reduces to an estimate of the quantity $\frac{1}{3}\omega_Q(q'/q)^2$. If we assume that a reasonable ratio of the modulated and principal z-components of the EFG tensor (q'/q) is 0.01–0.10 (Ref. 11), then at $\nu_Q\approx 30$ MHz (resonance of ^{35}Cl nuclei in organic-compound crystals) this coefficient ranges from 6×10^3 to 6×10^5 sec^{-1}, higher by several orders of magnitude than the analogous coefficient of F in the preceding section. Thus, in the case of relatively large values of Δ (compared with RT) the contribution of this mechanism to the relaxation is much larger than the contribution of the magnetic modulation mechanism. This circumstance leads to the conclusion that the foremost factor that must be taken into account in the interpretation of the relaxation data for quadrupole nuclei in crystals, in which there is unequal-well reorientational motion of atomic groups adjacent to these nuclei, are the fluctuations of the quadrupole interactions, i.e., the modulation of the EFG at the considered quadrupole nucleus.

3. EXPERIMENTAL RESULTS

The effect of unequal-well reorientation motion of a molecular fragment on the spin-lattice relaxation of a neighboring quadrupole nucleus was observed by us experimentally in the crystal $Cl_3P=NCCl(CF_3)_2$. We investigated in this compound the spectra of the quadrupole resonance of the ^{35}Cl nuclei that enter in the chemical bonds C–Cl and P–Cl (see Refs. 12 and 13 for the resonant frequencies of these nuclei at 77 K). The measured temperature dependences of the NQR frequencies and of the spin-lattice relaxation times obtained by using the procedure described in Ref. 14 are shown in Figs. 1 and 2.

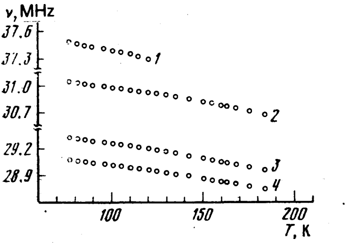

FIG. 1. Temperature dependence of NQR frequencies of ^{35}Cl in $Cl_3P=NCCl(CF_3)_2$ crystal: 1—C—Cl bond, 2–4—P—Cl bond.

For the chlorine nuclei in the C–Cl bonds we have observed above 77 K an exponential dependence of the time T_1 on the temperature (curve 1 of Fig. 2) and a fading of their resonance signal at $T\approx125$ K (Fig. 1), attesting to the presence in this crystal of a reorientational process, which may be only the reorientation of the asymmetrical fragment $CCl(CF_3)_2$ around the C–N bond. This is proved both by the behavior of the resonating chlorine nucleus in this fragment and by the behavior of the chlorine nuclei in the PCl_3 group, namely, the fact that the resonance signal fade for them only at a temperature near 190 K is evidence of the absence of reorientational motion of the entire molecule in the temperature interval 77–125 K of interest to us. An analysis of the results of NMR of ^{19}F (Ref. 6) has shown that at these temperatures there is likewise no noticeable CF_3-group motion capable of acting on the relaxation of the chlorine nuclei of the fragment $CCl(CF_3)_2$.

The specifics of the chemical structure of the $CCl(CF_3)_2$ fragment suggest that its reorientations have three equilibrium positions (rotational conformers), separated by potential barriers of different height. This agrees with the NMR data for ^{19}F (Ref. 6), which exhibit singularities typical of motion in an unequal-well potential[8,9]: unusually large values of T_1 (including $T_{1\min}$), and substantial delay of the observed temperature change of the second moment of the absorption line.

The plot of $T_1(T)$ for one of the chlorine nuclei in the PCl_3 group is shown by curve 2 of Fig. 2 [this curve corresponds to line 2 of Fig. 1; for the two other chlorine nuclei of the PCl_3 group the plots of $T_1(T)$ are similar and very close to curve 2]. The temperature dependence of T_1 in this case has a complicated character that can be attributed to a superposition of three relaxation mechanisms that made different contributions at different temperatures: 1) the libration relaxation

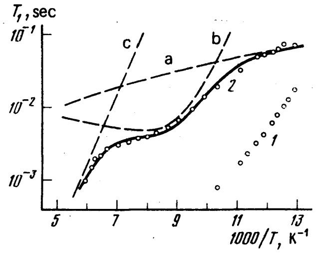

FIG. 2. Temperature dependence of time T_1 of spin-lattice relaxation for ^{35}Cl nuclei in $Cl_3P=NCCl(CF_3)_2$ crystal (the numbers correspond to those of Fig. 1). The solid curve 2 was calculated from expressions (16) and (17) using the parameters cited in the text. The points show the contributions made to T_1 by the liberation (a), modulation (b), and reorientation (c) relaxation mechanisms.

mechanism, which is the most effective at temperatures below ~85 K; 2) the modulation mechanism, which manifests itself in the region $80 < T < 130$ K, and 3) the reorientation mechanism (reorientation of the PCl_3 groups, which leads to vanishing of the NQR signal near 190 K), which prevails over the first two at $T > 130$ K. In this case

$$\left(\frac{1}{T_1}\right)_{\text{obs}}=\left(\frac{1}{T_1}\right)_{\text{libr}}+\left(\frac{1}{T_1}\right)_{\text{mod}}+\left(\frac{1}{T_1}\right)_{\text{reor}}$$
$$=aT^n+\left(\frac{1}{T_1}\right)_{\text{mod}}+b\exp\left(-\frac{V_0}{RT}\right), \qquad (16)$$

where V_0 is the potential barrier for the reorientations of the symmetrical group PCl_3 between the three equilibrium positions with identical potential energy.

The modulation mechanism of relaxation is undoubtedly due to the reorientational motion of the asymmetrical fragment $CCl(CF_3)_2$. To analyze the contribution of this mechanism to the relaxation rate of the chlorine nuclei of the P–C bonds we must know the shape of the potential surface for the reorienting asymmetrical fragment. It must first be assumed that the two metastable positions of the $CCl(CF_3)_2$ group are practically equivalent and their potential-well minima have identical energy; the potential well for the their position is deeper by an amount $\Delta \gg RT$, as follows directly from the NMR data for ^{19}F (Ref. 6). It can be furthermore assumed that the potential barriers between the equilibrium positions are produced to a considerable degree by intermolecular contacts between the given fragment and the chlorine atoms of the PCl_3 group of the neighboring molecule. This conclusion follows from the fact that the influence of the modulation on all three chlorine atoms in the PCl_3 group is the same, something that can hardly be expected in the case of predominantly intramolecular nonvalent interactions. The important role of the intermolecular nonvalent contacts in the formation of the potential barriers allows us to choose as the first approximation the very simple potential surface considered theoretically by Anderson[9]: one of the potential wells is Δ deeper than the other two, and the barriers that separate them have values E and $E+\Delta$. Then in accord with the exposition in Secs. 1 and 2 [Eq. (15) with account taken of (8), (9), and $\Delta \gg RT$], the modulation contribution to the relaxation rate (16) can be expressed in the form

$$\left(\frac{1}{T_1}\right)_{\text{mod}}=\frac{\omega_Q(q'/q)^2}{\exp(\Delta/RT)}\left\{\frac{3\omega_Q\tau_0\exp(E/RT)}{1+[\omega_Q\tau_0\exp(E/RT)]^2}+\frac{{}^1/{}_3\omega_Q\tau_0\exp(E/RT)}{1+[{}^1/{}_3\omega_Q\tau_0\exp(E/RT)]^2}\right\}, \qquad (17)$$

where $\omega_Q = 2\pi v_Q$ and v_Q is the resonant frequency of the ^{35}Cl nucleus in the P–Cl bond.

The parameters corresponding to Eqs. (16) and (17) can be obtained with a computer with sufficient accuracy. The solid curve 2 (Fig. 2), which describes the experimental points, was obtained for the following values of the parameters (relative error ~5%):

$$\omega_Q=2\pi\nu_Q=1.95\cdot10^8 \text{ sec}^{-1};$$
$$q'/q=0.05;$$
$$\tau_0=1.7\cdot10^{-13} \text{ sec};$$

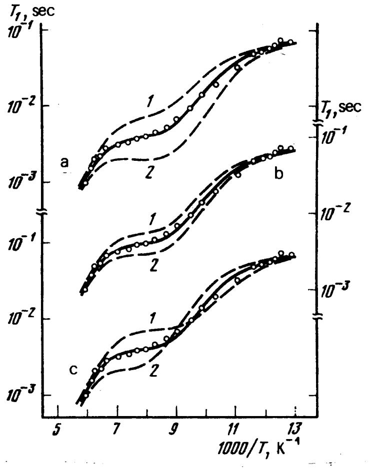

FIG. 3. Effect exerted in $T_1(T)$ by deviations from the optimal parameters cited in the text (solid curves), which determine $(T_1^{-1})_{\text{mod}}$ for the ^{35}Cl nuclei in the P—Cl bond. Curves 1 and 2 were calculated respectively for $\Delta = 2.14$ and 1.74 kcal/mole (a), 2.50 and 2.10 kcal/mole (b), and $q'/q = 0.04$ and 0.06 at optimal values of the remaining parameters.

$$E=2.30 \text{ kcal/mole};$$
$$\Delta=1.94 \text{ kcal/mole};$$
$$a=2.03\cdot10^{-3} \text{ sec}^{-1}\cdot\text{deg}^{-n};$$
$$n=2.05;\ b=1.1\cdot10^{9} \text{ sec}^{-1};$$
$$V_0=4.8 \text{ kcal/mole}.$$

The dashed curves in Fig. 2 show the contributions of the three individual relaxation mechanisms (16), corresponding to the given parameters. The obtained values of the parameters are reasonable, and the values of E, Δ, and τ_0 agree well with the values obtained from independent experiments. For example, the reduction of the $T_1(T)$ function for the chlorine nuclei in the C–Cl bonds (Fig. 2, curve 1) yields directly the value of the smallest potential barrier $E = 2.4 \pm 0.1$ kcal/mole; the values of E and Δ obtained from the reduction of the experimental data for the ^{19}F nuclei[6] are respectively 2.2 and 2.0 kcal/mole.

Figure 3 shows the influence of deviations from the optimal choice of the parameters E, Δ, and q'/q (which determine the modulation contribution to the rate of spin-lattice relaxation of the chlorine nuclei in the P–Cl bonds) on the accuracy of the approximation of the experimental data. As seen from the figure, the sensitivity to the choice of these parameters is very high and can serve as an estimate of the accuracy with which they are determined.

Thus, a theoretical analysis of the quadrupole modulation mechanism of spin-lattice relaxation in reorientation of a molecular fragment adjacent to a quadrupole nucleus and moving between unequal potential wells makes it possible to obtain the parameters that characterize the unequal-well reorientation process. The results of this analysis have made it possible to investigate, for the first time ever, the NQR method for an experimental study of reorientational motion of this type.

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Interaction potential between small neutral particles and spherical or cylindrical surfaces

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Exact expressions for the interaction potential of a neutral particle with the surfaces of a spherical particle or pore, of a cylindrical filament or channel in matter, is obtained on the basis of the general theory of van der Waals forces for arbitrary distances from the particle to the surface. Simple analytic expressions are obtained for the potential near the center of a pore or near the axis of a cylindrical channel, near the surfaces or at large distances from them, in the case when retardation is neglected, or in the opposite limiting case.

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The van der Waals interaction of neutral atoms, molecules, and small particles with condensed-phase surfaces is important for the calculation of many statistical and kinetic characteristics: the adsorption energies of individual atoms, the chemical potential of an adsorbed layer, the thermodynamics and kinetics of a gas in pores and capillaries in solids. For plane surfaces the potential was considered in Refs. 1 and 2. These calculations were used to obtain the adsorption energy of inert-gas atoms on plane metallic surfaces.[3] Since the curvature of the surface is essential in many cases (micropores, microcapillaries, small particles or filaments of radius $\sim 10^{-7}-10^{-5}$ cm), the dependences of the interaction potentials on the surface geometry were obtained for the particular case when the retardation is neglected.[4,5]

The purpose of the present paper is to construct the van der Waals interaction potential $U(r)$ of neutral molecules with spherical and cylindrical surfaces in the general case. We use here our earlier results on the thermodynamics of thin films on spherical and cylindrical surfaces,[6,7] and the reasoning proposed by Dzyaloshinskiĭ, E. Lifshitz, and Pitaevskiĭ[1] for planar surfaces.

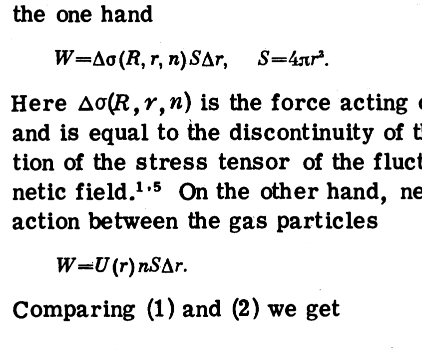
Consider, for example the interaction of molecules with a spherical particles of radius R (see the figure). We imagine that the molecules form a rarefied gas of density n, filling the volume of the space outside the sphere of radius r. The dielectric constant of this gas is $\varepsilon_3 = 1 + 4\pi\alpha n$. In a spherical layer of radii R and r we have vacuum ($\varepsilon_2 = 1$). The sphere of radius R has dielectric constant ε. Consider the work that the gas performs when its boundary is displaced by Δr. On the one hand

$$W = \Delta\sigma(R, r, n) S \Delta r, \quad S = 4\pi r^2. \tag{1}$$

Here $\Delta\sigma(R, r, n)$ is the force acting on a unit interface, and is equal to the discontinuity of the normal contention of the stress tensor of the fluctuating electromagnetic field.[1,5] On the other hand, neglecting the interaction between the gas particles

$$W = U(r) n S \Delta r. \tag{2}$$

Comparing (1) and (2) we get



a b

FIG. 1. a) Small particle with polarizability α at a distance r from the center of a sphere (from the axis of a cylinder) of radius R with dielectric constant E. b) The same particle inside a spherical (cylindrical) cavity of radius R in a medium with dielectric constant E.

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