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Nuclear magnetic resonance in lithium metal: Thermal mixing*

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We present a calculation of the thermal mixing rate τ_m^{-1} between nuclear Zeeman and dipolar reservoirs in the presence of large rf fields. We applied this calculation to slow-motion diffusion in lithium metal. In particular, we measured the rotating frame spin-lattice relaxation time $T_{1\rho}$ as a function of H_1 and observed the transition between the regions of validity of low-field and high-field theories. Furthermore, we demonstrated that this transition occurs when $T_{1\rho} \sim \tau_m$.

I. INTRODUCTION

It has long been known that a nuclear spin system in the presence of an rf field H_1 near its NMR frequency is characterized by a spin temperature in the rotating reference frame.[1,2] In an intense rf field (H_1 much larger than the local field H_L), the spins are quantized along H_1. In the next section of this paper, we demonstrate that this quantization results in the separation of the system into two parts, a Zeeman and a dipolar reservoir, each characterized by a spin temperature. We present a calculation of the thermal mixing rate τ_m^{-1} between these two parts and then apply it to slow-motion diffusion in lithium metal. In addition, we verify the results of this calculation by explicit measurement of the H_1 dependence of $T_{1\rho}$ of ^{7}Li in lithium metal.

II. THEORY

A. Thermal mixing

Consider a nuclear spin system[3] in a dc magnetic field $\vec{H}_0$ irradiated by an intense rf field $\vec{H}_1$ at a frequency ω near the NMR frequency $\omega_0 = \gamma H_0$. In a reference frame rotating about $\vec{H}_0$ with frequency ω, the time-independent "effective field" $\vec{H}_{\text{eff}}$ is given by

$$\vec{H}_{\text{eff}} = \vec{H}_1 + (H_0 - \omega/\gamma)\hat{H}_0 . \tag{1}$$

If we choose the z axis to be along $\vec{H}_{\text{eff}}$, the Hamiltonian can be written[2,4-7]

$$\mathcal{H} = \mathcal{H}_Z + \mathcal{H}_d^0 . \tag{2}$$

The first term $\mathcal{H}_Z$ is the Zeeman interaction between the spins and $\vec{H}_{\text{eff}}$ and is given, in units of frequency, by

$$\mathcal{H}_Z = -\gamma H_{\text{eff}} \sum_i I_{zi} . \tag{3}$$

The second term $\mathcal{H}_d^0$ is the secular dipolar interaction between spins and is time independent in the rotating reference frame. It can be broken into two parts: (i) $\mathcal{H}_d^{00}$ which is secular with respect to $\mathcal{H}_Z$ and (ii) $\mathcal{H}_d^{0n}$ which is nonsecular:

$$\mathcal{H}_d^0 = \mathcal{H}_d^{00} + \mathcal{H}_d^{0n} , \tag{4}$$

where

$$\mathcal{H}_d^{00} = \frac{1}{2}\left(\frac{3\cos^2\theta - 1}{2}\right)\sum_{i,j} A_{ij}(3I_{zi}I_{zj} - \vec{I}_i \cdot \vec{I}_j) \tag{5}$$

and

$$\mathcal{H}_d^{0n} = P + Q . \tag{6}$$

In the above,

$$P = \tfrac{3}{4}\sin^2\theta \sum_{i,j} A_{ij}(I_{xi}I_{xj} - I_{yi}I_{yj}) \tag{7}$$

and

$$Q = -3\sin\theta\cos\theta \sum_{i,j} A_{ij} I_{zi} I_{xj} . \tag{8}$$

θ is the angle between $\vec{H}_0$ and $\vec{H}_{\text{eff}}$, and A_{ij} is the usual dipolar coupling parameter given by

$$A_{ij} = \tfrac{1}{2}\gamma^2\hbar r_{ij}^{-3}(1 - 3\cos^2\theta_{ij}) . \tag{9}$$

In order to determine the form of the density operator, we rewrite the Hamiltonian by defining a unitary operator U such that

$$U\mathcal{H}_Z U^\dagger = \mathcal{H}_Z + \mathcal{H}_d^{0n} \equiv \mathcal{H}_Z^* . \tag{10}$$

We introduce an operator R defined by

$$U = e^{-iR} . \tag{11}$$

For $H_1 \gg H_L$, R will be small, and we can write to first order

$$\mathcal{H}_Z^* = \mathcal{H}_Z + i[\mathcal{H}_Z, R] . \tag{12}$$

From Eqs. (10) and (12), we obtain

$$i[\mathcal{H}_Z, R] = \mathcal{H}_d^{0n} , \tag{13}$$

which is used to evaluate R:

$$R = -\tfrac{3}{4}\sin^2\theta(\gamma H_{\text{eff}})^{-1}\sum_{i,j} A_{ij} I_{xi} I_{yj} + 3\sin\theta\cos\theta(\gamma H_{\text{eff}})^{-1}\sum_{i,j} A_{ij} I_{zi} I_{yj} . \tag{14}$$

Also, we have

$$\mathcal{H}_d^{00} = U^\dagger \mathcal{H}_d^{00*} U = \mathcal{H}_d^{00*} - i\,[\mathcal{H}_d^{00*}, R]\,. \tag{15}$$

Finally, from Eqs. (4), (10), and (15), we have[2]

$$\mathcal{H} = \mathcal{H}_Z^* + \mathcal{H}_d^{00*} - i\,[\mathcal{H}_d^{00*}, R]\,. \tag{16}$$

In Eq. (16), the first two terms, $\mathcal{H}_Z^*$ and $\mathcal{H}_d^{00*}$, commute, and the third term is smaller than either of the first two terms. Thus, $\mathcal{H}_Z^*$ and $\mathcal{H}_d^{00*}$ are quasiconstants of motion and can be described by separate spin temperatures β_Z and β_d. The density operator, in the high-temperature limit, is thus written

$$\sigma = 1 - \beta_Z \mathcal{H}_Z^* - \beta_d \mathcal{H}_d^{00*}\,. \tag{17}$$

Note that, although $\mathcal{H}_Z$ and $\mathcal{H}_d^{00}$ also commute, they are not quasiconstants of motion, since the remaining part of the Hamiltonian $\mathcal{H}_d^{0n}$ is not smaller than $\mathcal{H}_d^{00}$.

The third term in Eq. (16) is a small perturbation which causes β_Z and β_d to evolve towards a common spin temperature. We define the rate τ_m^{-1} of this thermal mixing by

$$\frac{d}{dt}(\beta_Z - \beta_d) = -\tau_m^{-1}(\beta_Z - \beta_d)\,. \tag{18}$$

From conservation of energy, we see that

$$\mathrm{Tr}(\mathcal{H}_Z^*)^2 \frac{d\beta_Z}{dt} + \mathrm{Tr}(\mathcal{H}_d^{00*})^2 \frac{d\beta_d}{dt} = 0\,. \tag{19}$$

From Eqs. (18) and (19) we have

$$\frac{d\beta_Z}{dt} = -\frac{\mathrm{Tr}(\mathcal{H}_d^{00*})^2}{\mathrm{Tr}\mathcal{H}^2}\frac{1}{\tau_m}(\beta_Z - \beta_d) \tag{20}$$

and

$$\frac{d\beta_d}{dt} = -\frac{\mathrm{Tr}(\mathcal{H}_Z^*)^2}{\mathrm{Tr}\mathcal{H}^2}\frac{1}{\tau_m}(\beta_d - \beta_Z)\,. \tag{21}$$

Using perturbation theory, τ_m^{-1} can be evaluated and is given by[2,4-7]

$$\tau_m^{-1} = \tau_{mQ}^{-1} + \tau_{mP}^{-1}\,, \tag{22}$$

where

$$\tau_{mQ}^{-1} = \left[1 + \frac{H_{\mathrm{eff}}^2}{H_L^2}\left(\frac{2}{3\cos^2\theta - 1}\right)^2\right]\langle\Delta\omega^2\rangle_{\mathrm{II}} \times \cos^2\theta\,\sin^2\theta\, J_Q(\gamma H_{\mathrm{eff}}) \tag{23}$$

and

$$\tau_{mP}^{-1} = \left[1 + \frac{H_{\mathrm{eff}}^2}{H_L^2}\left(\frac{2}{3\cos^2\theta - 1}\right)^2\right]\langle\Delta\omega^2\rangle_{\mathrm{II}} \times \sin^4\theta\, J_P(2\gamma H_{\mathrm{eff}})\,, \tag{24}$$

where $\langle\Delta\omega^2\rangle_{\mathrm{II}}$ is the Van Vleck second moment given by

$$\langle\Delta\omega^2\rangle_{\mathrm{II}} = 3I(I+1)\sum_j A_{ij}^2\,, \tag{25}$$

and H_L is the local field given by

$$H_L^2 = \mathrm{Tr}(\mathcal{H}_d^0)^2 \Big/ \gamma^2\,\mathrm{Tr}\Big(\sum_i I_{zi}\Big)^2 = \tfrac{1}{3}\gamma^{-2}\langle\Delta\omega^2\rangle_{\mathrm{II}}\,. \tag{26}$$

The spectral density functions $J_Q(\omega)$ and $J_P(\omega)$ are given by

$$J_Q(\omega) = \int_0^\infty d\tau\,\cos(\omega\tau)\,G_Q(\tau)\,, \tag{27}$$

and

$$J_P(\omega) = \int_0^\infty d\tau\,\cos(\omega\tau)\,G_P(\tau)\,. \tag{28}$$

$G_Q(\tau)$ and $G_P(\tau)$ are correlation functions given by

$$G_Q(\tau) = \mathrm{Tr}[Q(\tau)\,Q]/\mathrm{Tr}Q^2 \tag{29}$$

and

$$G_P(\tau) = \mathrm{Tr}[P(\tau)\,P]/\mathrm{Tr}P^2\,, \tag{30}$$

where

$$Q(\tau) = \exp(i\mathcal{H}_d^{00}\tau)\,Q\,\exp(-i\mathcal{H}_d^{00}\tau) \tag{31}$$

and

$$P(\tau) = \exp(i\mathcal{H}_d^{00}\tau)\,P\,\exp(-i\mathcal{H}_d^{00}\tau)\,. \tag{32}$$

It is straightforward to show that

$$Q(\tau) = -2i\,\sin\theta\,\cos\theta\,(3\cos^2\theta - 1)^{-1}\Big[\mathcal{H}_d^{00}, \sum_i I_{yi}\Big]\,. \tag{33}$$

Substituting this into Eq. (29), we get that

$$G_Q(\tau) = \frac{\mathrm{Tr}\big([\mathcal{H}_d^{00}, \sum_i I_{yi}][\mathcal{H}_d^{00}, \sum_i I_{yi}(\tau)]\big)}{\mathrm{Tr}\,[\mathcal{H}_d^{00}, \sum_i I_{yi}]^2}\,. \tag{34}$$

Finally, $G_Q(\tau)$ can be written in the form[4,6]

$$G_Q(\tau) = -\frac{1}{\langle\Delta\omega^2\rangle_{\mathrm{II}}} G''_{\mathrm{FID}}\left(\frac{3\cos^2\theta - 1}{2}\tau\right)\,, \tag{35}$$

where $G''_{\mathrm{FID}}(t)$ is the second time derivative of the normal free-induction-decay envelope given by[8]

$$G_{\mathrm{FID}}(t) = \frac{\mathrm{Tr}\big[(\sum_i I_{xi})\exp(i\mathcal{H}_d^0 t)(\sum_i I_{xi})\exp(-i\mathcal{H}_d^0 t)\big]}{\mathrm{Tr}(\sum_i I_{xi})^2}\,. \tag{36}$$

From Eqs. (27) and (35), we obtain

$$J_G(\omega) = \pi\left|\frac{2}{3\cos^2\theta - 1}\right|^3 \frac{\omega^2}{\langle\Delta\omega^2\rangle_{\mathrm{II}}}\, g\left(\frac{2\omega}{3\cos^2\theta - 1}\right)\,, \tag{37}$$

where $g(\omega)$ is the normalized NMR absorption signal shape given by

$$g(\omega)=\frac{1}{\pi}\int_0^\infty d\tau\cos(\omega\tau)\,G_{\mathrm{FID}}(\tau)\,. \tag{38}$$

Using Eq. (23), we finally have[2,4,6,9]

$$\tau_{mQ}^{-1}=\left[1+\frac{H_{\mathrm{eff}}^2}{H_L^2}\left(\frac{2}{3\cos^2\theta-1}\right)^2\right]\pi\sin^2\theta \times\cos^2\theta\left|\frac{2}{3\cos^2\theta-1}\right|^3\gamma^2H_{\mathrm{eff}}^2\,g\left(\frac{2\gamma H_{\mathrm{eff}}}{3\cos^2\theta-1}\right). \tag{39}$$

A nice feature of the above equation is that it is quite general and has not required any assumptions about the explicit functional form of either the correlation function or the line shape.

The expression for τ_{mP}^{-1} involves $G_P(\tau)$ which cannot be simply related to the line shape in the same way as can $G_Q(\tau)$. As a result, the expression for τ_{mP}^{-1} cannot be similarly simplified without assumptions about the explicit form of $G_P(\tau)$. An approximation can be made, however, by assuming the form of $G_P(\tau)$ to be Gaussian[5,7]

$$G_P(\tau)=\exp(-\tau^2/\tau_C^2)\,. \tag{40}$$

The correlation time τ_C can be evaluated[5] by taking a power expansion of $G_P(\tau)$ and equating coefficients of τ^2,

$$\tau_C^{-2}=-\frac{1}{2}\frac{d^2}{d\tau^2}G_P(\tau)\bigg|_{\tau=0}=\frac{-\frac{1}{2}\mathrm{Tr}[P,\mathcal{H}_d^{00}]^2}{\mathrm{Tr}P^2}$$

$$=\tfrac{2}{3}\left(\frac{3\cos^2\theta-1}{2}\right)^2\langle\Delta\omega^2\rangle_{\mathrm{II}}\left[1+\frac{\left(2\sum_{j,k}A_{ij}A_{ik}A_{jk}^2-\{\frac{2}{5}+\frac{9}{20}[1/I(I+1)]\}\sum_j A_{jk}^4\right)}{(\sum_j A_{ij}^2)^2}\right]. \tag{41}$$

From Eqs. (24), (28), and (40), we have

$$\tau_{mP}^{-1}=\left[1+\frac{H_{\mathrm{eff}}^2}{H_L^2}\left(\frac{2}{3\cos^2\theta-1}\right)^2\right]\tfrac{1}{2}\sqrt{\pi}\sin^4\theta \times\langle\Delta\omega^2\rangle_{\mathrm{II}}\tau_C\exp(-\gamma^2H_{\mathrm{eff}}^2\tau_C^2)\,. \tag{42}$$

For H_1 off-resonance ($\theta\neq\frac{1}{2}\pi$), the rate τ_{mQ}^{-1} dominates the thermal mixing due to the fact that $J_P(2\gamma H_{\mathrm{eff}})$ is smaller than $J_Q(\gamma H_{\mathrm{eff}})$ since the argument $2\gamma H_{\mathrm{eff}}$ of J_P is further out in the wings. This case has been investigated by Clough[10] in CaF_2. The experimental values for τ_m^{-1} were found to be in good agreement with theory. Einbinder and Hartman[11] also observed thermal mixing in CaF_2.

For H_1 on resonance ($\theta=\frac{1}{2}\pi$), the rate τ_{mP}^{-1} dominates the thermal mixing, since $\cos\theta=0$. This case has been investigated by Mansfield and Ware[5] in CaF_2. They found that experimental determination of τ_m^{-1} for this case was very difficult, giving only order of magnitude estimates.

We too investigated this case ($\theta=\frac{1}{2}\pi$) by measuring $T_{1\rho}$ of ^7Li in lithium metal. The details of this experiment are given in the following sections of this paper.

B. Application to diffusion in lithium metal

Diffusion in lithium metal strongly affects $T_{1\rho}$ over a certain temperature range.[12,13] According to the Slichter-Ailion theory, the contribution of diffusion to $T_{1\rho}$ for small H_1 on resonance is given by

$$T_{1\rho,\,\mathrm{diff}}=[(H_1^2+H_L^2)/H_L^2]\,T_{1D\ \mathrm{diff}}\ , \tag{43}$$

where T_{1D} is the dipolar relaxation time, the limiting case of $T_{1\rho}$ for $H_1=0$.

For large H_1, we must consider the relaxation of the Zeeman and dipolar parts separately, as can be seen from Eq. (17). In the absence of spin-lattice relaxation, Eqs. (20) and (21) give, for H_1 on resonance ($\theta=\frac{1}{2}\pi$),

$$\frac{d\beta_Z}{dt}=-\frac{\frac{1}{4}H_L^2}{H_1^2+H_L^2}\frac{1}{\tau_m}(\beta_Z-\beta_d) \tag{44}$$

and

$$\frac{d\beta_d}{dt}=-\frac{H_1^2+\frac{3}{4}H_L^2}{H_1^2+H_L^2}\frac{1}{\tau_m}(\beta_d-\beta_Z)\,. \tag{45}$$

If we add the relaxation rate due to diffusion,[13] we obtain

$$\frac{d\beta_Z}{dt}=-\frac{\frac{1}{4}H_L^2}{H_1^2+H_L^2}\frac{1}{\tau_m}(\beta_Z-\beta_d)-\frac{\frac{3}{4}H_L^2}{H_1^2+\frac{3}{4}H_L^2}\frac{1}{T_{1D,\,\mathrm{diff}}}\beta_Z \tag{46}$$

and

$$\frac{d\beta_d}{dt}=-\frac{H_1^2+\frac{3}{4}H_L^2}{H_1^2+H_L^2}\frac{1}{\tau_m}(\beta_d-\beta_Z)-\frac{1}{T_{1D,\,\mathrm{diff}}}\beta_d\,. \tag{47}$$

In the last term of Eq. (47), there is no explicit field dependence since the field-dependent terms in the numerator and denominator of Eq. (43) cancel in this case.

Solving Eqs. (46) and (47) with the initial condition, $\beta_Z(0)\gg\beta_d(0)$, we obtain

$$\beta_z(t) = \beta_z(0) \exp(-t/T_{1\rho,\,\mathrm{diff}}) . \tag{48}$$

The expression for $T_{1\rho,\,\mathrm{diff}}$ can be written in simple form for two limiting cases. First, if H_1 is sufficiently small such that thermal mixing is fast and $\beta_z = \beta_d$, we have Eq. (43). Second, for large H_1, such that thermal mixing is slow and can be neglected, we have[13]

$$\frac{1}{T_{1\rho,\,\mathrm{diff}}} = \frac{\frac{3}{4}H_L^2}{H_1^2 + \frac{3}{4}H_L^2}\,\frac{1}{T_{1D,\,\mathrm{diff}}} . \tag{49}$$

The region of transition between these two limiting cases occurs where $\tau_m \sim T_{1\rho,\,\mathrm{diff}}$.

If we plot $T_{1\rho,\,\mathrm{diff}}$ as a function of H_1^2, we should get a straight line for each limiting case but with different slopes. Ailion[14] attempted to see this change of slope in lithium metal but was unsuccessful because of experimental scatter attributed to unstable temperature control at large H_1. Messer, Dais, and Wolf[15] measured $T_{1\rho}$ at various values of H_1 in aluminum metal, but the published experimental details are too incomplete for analysis in terms of thermal mixing rates.

III. EXPERIMENT

We measured $T_{1\rho}$ at various values of H_1 $(\omega_0/2\pi = 24$ MHz) at two different temperatures (see Figs. 1 and 2). The contribution to $T_{1\rho}$ from conduction electrons had to be subtracted off in order to obtain $T_{1\rho,\,\mathrm{diff}}$. Relaxation due to conduction electrons in a metal is given by[16,17]

$$T_{1\rho,e} = [(H_1^2 + H_L^2)/(H_1^2 + \alpha H_L^2)]\, T_{1,e} . \tag{50}$$

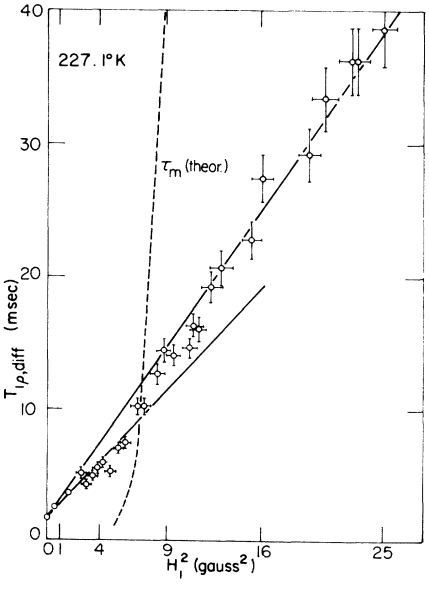

FIG. 1. $T_{1\rho,\mathrm{diff}}$ in powdered lithium metal at 227.1 °K as a function of H_1^2. Solid lines are best fits with the data consistent with Eqs. (43) and (49). Dashed line is τ_m from Eq. (53) with no adjustable parameters.

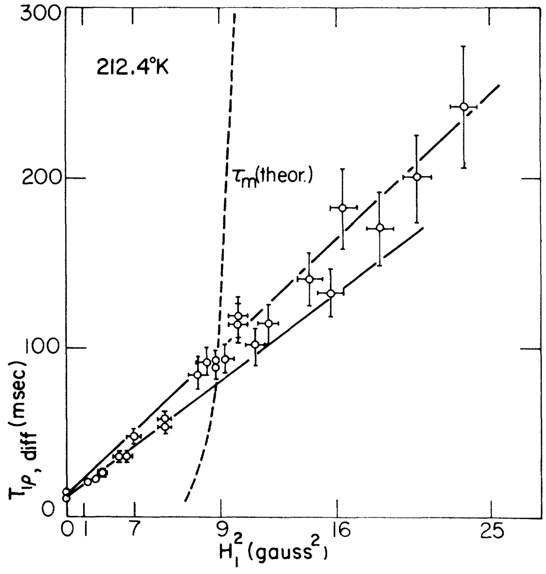

FIG. 2. $T_{1\rho,\mathrm{diff}}$ in powdered lithium metal at 212.4 °K as a function of H_1^2. Solid and dashed lines have the same meaning as in Fig. 1.

From the Korringa relationship,[16,17] we have

$$T_{1,e} = K/T , \tag{51}$$

where $K = 44$ s °K. At 162 °K, (well outside the diffusion region) we measured $T_1 = 260$ msec. and $T_{1D} = 150$ msec. This agrees with Eq. (51) and gives us $\alpha = 1.7$. Using Eq. (50) and (51), we obtained $T_{1\rho,\,\mathrm{diff}}$ from[16]

$$T_{1\rho,\,\mathrm{diff}}^{-1} = T_{1\rho}^{-1} - T_{1\rho,e}^{-1} . \tag{52}$$

Examination of Figs. 1 and 2 shows a definite change of slope in the data as we go from small H_1 to large H_1. The solid lines shown are the best fits to the data consistent with Eqs. (43) and (49).

From Eq. (42), we can calculate the thermal mixing rate for powdered lithium metal and obtain

$$\tau_m = \frac{(\frac{1}{2}\sqrt{\pi}\langle\Delta\omega^2\rangle_{\mathrm{II}}\tau_C)^{-1}}{1 + (4/H_L^2)H_1^2} \exp(\gamma^2\tau_C^2 H_1^2) , \tag{53}$$

where

$$(\tfrac{1}{2}\sqrt{\pi}\langle\Delta\omega^2\rangle_{\mathrm{II}}\tau_C)^{-1} = 24\,\mu\mathrm{s} ,$$

$$4/H_L^2 = 2.8\ \mathrm{G}^{-2}, \quad \text{and} \quad \gamma^2\tau_C^2 = 1.28\ \mathrm{G}^{-2} .$$

This is shown as a dotted line in Figs. 1 and 2 and intersects the data at approximately the transition region as we predicted.

IV. CONCLUSION

In this paper, we have verified experimentally the prediction that the dependence of $T_{1\rho,\,\mathrm{diff}}$ on H_1^2 should change slope by a factor of $\frac{4}{3}$ when H_1 becomes sufficiently large to prevent thermal mixing in a time comparable to $T_{1\rho,\,\mathrm{diff}}$. Furthermore, we observe the change of slope to occur, as predicted, when $\tau_m \sim T_{1\rho,\,\mathrm{diff}}$. This agreement suggests that our assumption of a Gaussian correlation function leads to the correct value of τ_m.

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$$W=\pi \sin^2\theta \cos^2\theta \left|\frac{2}{3\cos^2\theta-1}\right|^3 \omega_e^2 g\left(\frac{2\omega_e}{3\cos^2\theta-1}\right).$$

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