学位申請論文

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Dipole of Centrosymmetric Dimer of Fatty Acid : Limitation of
the Vector Sum Law.

（対称系である脂肪酸二量体の双極子；ベクトル和則の適用限界）

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（論文内容の要旨）

　一般に対称な分子あるいは分子系は，ベクトル和則により電気双極子を持たず，誘電緩和を起こさないと考えられている。しかしながら，ベクトル和則は厳密には各瞬間の双極子系にのみ成立するのに対し，誘電緩和を起こす双極子は，ほぼ緩和時間程度の長さにわたって統計平均されたものである。したがって対称系でも双極子を持ち得ることになる。本論文は，対称系である脂肪酸二量体が双極子を持つことを実験的に見出し，その双極子の成立機構を論じたものである。

　申請者は，undecanoic acid, tridecanoic acid, pentadecanoic acid, （以上，奇数脂肪酸）dodecanoic acid, tetradecanoic acid, hexadecanoic acid, （以上，偶数脂肪酸）などの，脂肪酸を取り上げ，二量体を構成している固体状態で誘電測定を行った。ここに測定した固体脂肪酸は，プラスチックフローを起こし熱膨張も大きいため，試料の厚さが変化し，正確に誘電率を測定することは一般に困難である。申請者は試料の厚さと電気容量を同時測定できる電極を工夫製作し使用することにより，正確な誘電率値を得ている。また再結晶によって試料の精製を行い，純度をガスクロマトグラフィーおよび融点測定により確かめている。誘電測定の結果，三種類の奇数脂肪酸において誘電緩和を見出し，いずれの緩和も緩和周波数が温度上昇とともに高周波側に移動すること，および通常の双極子による緩和と異なり緩和強度が温度上昇と共に大きくなることを観測した。さらに偶数脂肪酸の測定では誘電緩和が認められなかった。

　これらの実験結果を説明するために，申請者は，この現象がヤーン・テラー効果によるものではないと考え，次のような双極子生成機構を提案している。個々の双極子は互いにある程度の相関を持って運動している。この運動は周囲からの無秩序な力や結晶場などにより攪乱されている。この攪乱が二つの双極子を結ぶ力（脂肪酸の場合は水素結合）に比べて大きい場合には、両双極子の運動は相関を失う。相関が小さくなると双極子は個別に電場と相互作用する性質を持ち始める。その結果，系全体としては双極子モーメントを生じる。さらに，この考えを定量化し，立式して，両双極子間相対運動の位相遅れを表すパラメーターを導入して計算を進めている。

その結論として，両双極子を含む全体の統計平均モーメントの大きさが位相遅れに比例することを示した。この機構で生じた双極子は，その方向が一定であり，大きさが時間的に変化することも導かれた。さらに，双極子モーメントの理論値は実験値と良く一致した。誘電緩和が奇数脂肪酸で観測され，偶数脂肪酸では観測されなかった事実は，結晶形の違いにより偶数脂肪酸では，水素結合が強く，運動の相関も失われず，位相遅れも小さいためであると結論している。

　参考論文10編は，おもに誘電的研究である。

（論文審査の結果の要旨）

　　対称な分子系は双極子を持たないと考えられている。しかし，分子系が内部的に運動している場合には，この考えは必ずしも成り立たない。本論文において申請者は，信頼性の高い測定方法を開発し，誘電緩和の温度依存性などを実験観察し，さらにこれらの実験結果に対して，合成双極子モーメントの生じる動的モデルを提案している。このモデルは，対称系のみならず分子系一般に広く適用できるものであり，分子，原子運動の研究を大きく進展させることが期待できる。

　　脂肪酸の誘電的性質に関しては，すでに幅広い関心が寄せられているが，従来は，完全な対称系ではないような液体状態の研究が主であった。申請者は，完全な対称系と考えられる二量体脂肪酸類の固体状態での誘電測定を行い，三種類の奇数脂肪酸について誘電緩和を見出した。これにより，対称系でも双極子を持ち得ることを実験的に見出した。また誘電測定については，試料の形状と電気容量を同時に測定できるような電極を製作し，変形の大きい脂肪酸固体についても正確な誘電率と誘電損失を得ることが出来るようになった。このように新しく開発された電極を含む測定系は，精密な誘電率測定法として，重要な意味を持つ。申請者は，実験結果の解析に当り，分子系が内部運動している場合，長い時間域に対しては，ベクトル和則が成立しないことを理論的に明らかにした。これを推し進め，従来は対称と考えられていた系においても双極子モーメントが生じるようなモデルを提案した。このモデルは，ヤーン・テラー効果に依るものではなく，新しい着想に基ずくものである。今後このモデルに基づく理論的双極子モーメントが他の実測例においても発見され，双極子の運動に関する研究が大きく発展するものと思われる。このモデルは奇数脂肪酸と偶数脂肪酸の性質の違いをも良く説明し，充分に妥当なモデルである。申請者は，さらに結晶形と関連づけて水素結合を論じ，結晶形や水素結合の強さが，どのように誘電的性質に反映するかを明らかにした。このことにより，水素結合の研究に対しても価値ある寄与をなしている。

　　以上に述べたように，申請論文は，脂肪酸類の固体状態に於ける誘電特性につ

いて，多くの重要な実験結果を提示し，これに新しい理論的解釈を与えたものであり，当該研究分野に寄与するところは大きい。

　参考論文10編は，おもに誘電的性質の研究であり，申請者のこの分野における広い学識を示すものである。

　したがって本論文は，理学博士の学位論文として価値あるものと認める。

　なお，主論文及び参考論文に報告されている研究業績を中心として，これに関連した研究分野について試問した結果，合格と認める。

Dipole of Centrosymmetric Dimer of Fatty Acid: Limitation of the Vector Sum Law.

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Dielectric relaxations were found in the centrosymmetric systems of the odd numbered fatty acid dimers of undecanoic, tridecanoic, and pentadecanoic acids, while not detected in even numbered acid dimers of lauric, myristic and palmitic acids. These dielectric relaxations suggest that the dipole of a symmetric system is not always zero, though the fatty acid dimers have been assumed to possess no dipole because of the existence of a center of symmetry. It is shown that the vector sum law for electric dipoles has a limitation. A model having the dipole caused by phase shift between rotational motions of two anti-parallel dipoles in the symmetric dimer was proposed. The phase shift is produced by random forces of neighboring dimers, when the forces are strong enough in comparison with the hydrogen bond strength in the dimer. In the proposed model, the dipole is expressed by a single parameter of the phase shift and changes its magnitude but not its direction. The difference in dielectric properties between odd and even numbered acids was explained by the difference in strength of hydrogen bonds which was strongly correlated with the crystal packing. The strong hydrogen bond, which correlates to the C-form crystal packing, of even numbered acids forms no net dipole cancelling the two anti-parallel dipoles each other. However, the hydrogen bond of odd numbered acids are weak owing to the different crystal packing. In the weak hydrogen bond the monomeric movement in the dimer can be caused by the strong disturbance and derives a dipole in the symmetric dimer unit.

Introduction

The Stark effect observed in T_d symmetric methane molecule[1,2] shows that a permanent or a long life dipole exists in some symmetric molecules and suggests that the vector sum law for the dipole has some limitation. The dielectric study of dipole detection in symmetric system is necessary to examine the limitation of the vector sum law for the dipole. The mechanism proposed by Mizushima and Venkateswarlu[3] (one kind of the Jahn-Teller effect) for the dipole formation in a T_d symmetric molecule can not be applied to that in the C_{2h} symmetry system as proved by Mills, Watson, and Smith.[4] Though the theory of Mizushima and Venkateswarlu is valid for an isolated molecule in gaseous phase, the atomic motions in a molecule are disturbed in condensed phase with random forces from the neighboring molecules and the C_{2h} symmetry molecule may have a dipole as a consequence. The search of dipoles in C_{2h} symmetry such as fatty acid dimer is desired for the check of limitation of vector sum law. Several investigations[5,6,7] on the dielectric properties of liquid fatty acids suggest the existence of the dipole, though the liquid fatty acids are almost completely associated into dimers. However, these investigations did not discuss on the limitation of vector sum law for the dipole. Smyth and Rogers[5] observed the anomaly that the permittivity of liquid acetic acid increases with increasing temperature and they ascribed the anomaly to the monomer-dimer equilibrium. The idea that the fatty acid dimer unit possesses a dipole was first introduced by Harris and Alder[6] with the ion pair model. Later Loveluck[7] discarded the ion pair model which yielded abnormally large dipole moment as well as activation energy. He estimated the dipole moment of n-caproic acid dimer as 0.7 D, but the origin of dipole was not sufficiently explained. Fatty acids in solid state form the dimers completely and those crystal structures are well known,[8,9] whereas in liquid state the dimer formation is incomplete. The detection of a dielectric relaxation in solid fatty acids proves the existence of a dipole in a perfect dimer. Dielectric properties of solid fatty

acids have been little measured. Since the specimen thickness varies[10] considerably owing to the plastic flow and the large thermal expansion of the substance, it is hard to estimate the thickness and consequently the permittivity accurately. The dielectric cell constructed by McCammon and Work[11] and improved by the author[12] is designed for the in situ measurement of the specimen thickness and thus suitable to measure the dielectric properties of fatty acid plastic crystal. The purpose of this work is to detect the dipole in the C_{2h} symmetric system and to discuss the origin of the dipole. The difference in physical properties between odd and even numbered fatty acids may give some hints to the origin of the dipole. The odd numbered acids show reversible phase transitions[8] of the form $C' \leftrightarrow A'$ for tridecanoic acid and the form $C' \leftrightarrow B'$ for undecanoic and for pentadecanoic acid, while the even numbered acids keep a single phase[8] (the C-form) in a wide temperature range. The strength of the hydrogen bond changes considerably with the crystalline phase. The difference in the hydrogen bond may give the difference in the dielectric properties of solid fatty acids, showing the possibility of the dipole in a symmetrical dimer unit.

Experimental.

Commercial reagents of undecanoic acid $C_{10}H_{21}COOH$, tridecanoic acid $C_{12}H_{25}COOH$, pentadecanoic acid $C_{14}H_{29}COOH$, lauric acid $C_{11}H_{23}COOH$, myristic acid $C_{13}H_{27}COOH$, and palmitic acid $C_{15}H_{31}COOH$ were purified by recrystallization over seven times from methanol or n-hexane. The specimens were dried in vacuum for several hours and kept in dry nitrogen. The purities of these acids over 99.8 % were checked by melting point and gas chromatography. Although voids were frequently introduced into the sample at the sample setting in the dielectric cell, these voids can be removed by the plastic flow of the compounds[12] as follows. The cell, in which the sample was weakly stressed, was kept just below the melting point over three weeks till no permittivity change was observed for a day. The permittivity and the specimen thickness were measured simultaneously with the dielectric cell described before[12] by the use of a YHP Co. 4274A LCR meter and an Ando Electric Co. TR-10 transformer bridge. Extremely low loss of pentadecanoic acid was measured by a General Radio Co. 1616 transformer bridge. The cryostat has been described before.[12] The cooling rate was 0-0.07 Ks^{-1} and the heating rate 0-0.03 Ks^{-1}. After the dielectric measurement the orientation of the crystal axis was determined by the X-ray diffraction for the samples on the electrode with a Rigaku Denki Co. RU-3 X-ray diffractometer. Numerical calculations were carried out with a Facom M-380-Q Computer in the Institute and a Facom M-382 Computer in the Data Processing Center of Kyoto University.

Results

Dielectric relaxations were observed from 150 K to 250 K in the low temperature phase for odd numbered fatty acids of undecanoic, tridecanoic, and pentadecanoic acid as shown in Figures 1-3. Figure 1 demonstrates the plots of the imaginary parts of relative permittivity against frequency for the B'-form[8] of undecanoic acid around 210 K where dielectric relaxation is clearly seen. No difference was observed between heating and cooling processes. The relaxation intensity, which was estimated with the loss data,[13] increases with temperature. Dipole moments of the relaxation estimated using Onsager's equation[14] are shown in Table I. Figure 2 represents the plots of the imaginary parts of relative permittivity against frequency for the A'-form of tridecanoic acid around 170 K. Dielectric relaxation was also observed. The dipole moments determined as above are also listed in Table I. Figure 3 displays the imaginary parts for the B'-form of pentadecanoic acid around 220 K. Dielectric relaxation is observed, although the relaxation intensity was too small to determine the dipole moment for pentadecanoic acid.

Real parts of relative permittivities of odd numbered acids in the temperature range from liquid nitrogen temperature to the melting point are given in Figures 4-6. The values of relative permittivities below 200 K were almost constant around 2.27 for the B'-form of undecanoic acid, 2.33 for the A'-form of tridecanoic acid, and 2.34 for the B'-form of pentadecanoic acid as seen in Figures 4, 5 and 6, respectively. The change of the permittivities was reversible in the cooling or heating cycle in this low temperature region. Around the transition temperature, the permittivity of undecanoic acid increased discontinuously at 281 K on cooling and decreased at 291 K on heating. The permittivity of tridecanoic and pentadecanoic acid decreased opposite to that of the undecanoic acid at 292 K and 306 K on cooling, respectively and increased at 306 K and 319 K on heating, respectively. Thermal hysteresis loops were observed around the transition

temperature. The frequency dependence of the permittivity near the respective transition temperatures may be explained by the Curie-von Schweidler law.[16]

Real parts of relative permittivities for the C form of even numbered acids from liquid helium temperature to the melting point are given in Figures 7-9. The permittivity of lauric acid decreases from 2.8 to 2.4 by cooling or increases by heating as seen in Figure 7. The permittivities are a little larger than the Gough's results.[17] The value in heating process is almost constant in the temparature range from 80 K to 250 K, but increases in higher temperature range over 250 K and eventually returns to the original value 2.8 before cooling. The thermal hysteresis loop was observed. The permittivities of the C-form of myristic acid or that of palmitic acid were almost constant about 2.50-2.55 or 2.41-2.43, respectively, as shown in Figures 8 and 9, though thermal hysteresis loops were again observed in the magnified scale. The dispersions of the Curie-von Schweidler law were also observed several tens of degrees below the melting points. The dielectric relaxations found in the low temperature phase of odd numbered acids were not observed in even numbered acids. After the dielectric measurement the sample sticked solidly to the electrodes. When an electrode was separated from the sample after many attempts, the X-ray diffraction of the sample on the other electrode gave very strong (00𝑙) reflections and very weak (110) reflection, suggesting that the crystalline ab-plane was perpendicular(c-axis was nearly parallel) to the electric field.

Discussion

Origin of the dipole. A mechanism is discussed to cause the dielectric relaxation found in a centrosymmetric system. The dielectric relaxation intensities due to polar impurities should decrease[18] with temperature. Since the relaxation intensities observed in the C_{2h} symmetric system of odd numbered acid dimers increase with temperature, the dielectric relaxations are not due to a polar impurity such as water. We propose a model that the symmetric dimer itself possesses a dipole. The dipole derived theoretically by Mizushima and Venkateswarlu[3] in a symmetric system can not[4] exist in the C_{2h} fatty acid dimer. In the model a dipole arises from a different mechanism from Mizushima and Venkateswarlu's theory. The one dimer approximation is adopted i.e. one dimer is isolated in the continuous medium and the atomic motions within the dimer are specified by random and interatomic forces in the crystal field. A model calculation is performed for the dipole moment per dimer unit and the dielectric properties of the substance are determined by an average of dimer ensemble. Three states of the dimer are considered as follows: If the monomer-monomer interaction in a dimer unit is very strong (a perfect dimer state), one monomer can not move independently of the other monomer. Though the dipole can be instantaneously induced in the dimer, the dipole averaged during a long period is zero. The dielectric relaxation can not be observed in this case, because the dielectric relaxation is caused by the averaged dipole. If the monomer-monomer interaction is negligible(a perfect monomer state), a monomer moves independently of the other to cause the dielectric relaxation by its permanent dipole. If the monomer-monomer interaction is moderate (a quasi-dimer state), the dimer possesses a smaller dipole monomer, because of the non-correlated motion of the monomer unit. The fatty acids under investigation seem to be in the quasi-dimer state specified by the moderate monomer-monomer interaction.

Figure 10 illustrates the directions of monomer dipoles at an instant in the

molecule(dimer)-fixed Cartesian coordinates. Capital letters of C, H, and O denote the average positions of atoms in equilibrium. The z axis is defined to be parallel to the long axis of dimer. The x-z plane is in the carboxylic ring plane. The dipole μ_1 of the monomer 1 at an instant crosses the z axis at an angle θ_1 and the projection of μ_1 on the x-y plane forms an angle φ_1 with x axis. The direction of the dipole μ_2 of the monomer 2 is defined as the same. The dipoles μ_1 and μ_2 are expressed as

$$\mu_1 = \mu(\sin\theta_1\cos\varphi_1, \ \sin\theta_1\sin\varphi_1, \ \cos\theta_1),$$

$$\mu_2 = \mu(\sin\theta_2\cos\varphi_2, \ \sin\theta_2\sin\varphi_2, \ \cos\theta_2),$$

where μ is the magnitude of a monomer dipole. The vector sum law holds in short time scale and gives the instantaneous dipole $\mu_1 + \mu_2$ for the dimer as

$$\mu_1 + \mu_2 = \mu(\sin\theta_1\cos\varphi_1 + \sin\theta_2\cos\varphi_2, \ \sin\theta_1\sin\varphi_1 + \sin\theta_2\sin\varphi_2, \ \cos\theta_1 + \cos\theta_2), \tag{1}$$

When the monomer-monomer interaction is very strong, θ_2 and φ_2 can be expressed in terms of θ_1 and φ_1 as

$$\theta_2 = \pi - \theta_1, \qquad \text{and} \qquad \varphi_2 = \varphi_1, \tag{2}$$

In this case the dimer has no averaged dipole:

$$\langle \mu_1 + \mu_2 \rangle = 0,$$

where $\langle\ \rangle$ denotes the average over a long period. When the monomer-monomer interaction is very weak, θ_1, θ_2, φ_1, and φ_2 are independent variables, and the average of the dimer dipole is expressed in terms of the sum of the individual monomer dipoles as

$$\langle \mu_1 + \mu_2 \rangle = \langle \mu_1 \rangle + \langle \mu_2 \rangle,$$

where an electric field interacts with the dipole of the monomer. The real state of the substance is in the intermediate between monomer and dimer. The correlated motions in the dimer are disturbed with random forces from surroundings. To express the non-correlated portion of the monomer movement in eq 2, we introduce the random variables δ and ε as the phase shifts of angles :

$$\theta_2 = \pi - (\theta_1 + \delta) \qquad \text{and} \qquad \varphi_2 = \varphi_1 - \varepsilon \tag{3}$$

The phase shifts in the dipole motion are caused by the disturbance of random forces. These phase shifts serve as the measure of the monomeric character in the dimer and of the strength of disturbance. The large phase shifts denote a strong disturbance and a dominant monomeric character. These phase shifts are introduced as parameters, though these can in principle be calculated from the correlation function between two monomers. Since the monomer-monomer interaction is considerably strong in comparison with the disturbance, the phase shifts δ and ε are assumed to be small. The insertion of eq 3 into eq 1 gives the instantaneous dipole of

$$\mu_1+\mu_2=\mu(\sin\theta\cos\varphi+\sin(\theta+\delta)\cos(\varphi-\varepsilon), \ \sin\theta\sin\varphi+\sin(\theta+\delta)\sin(\varphi-\varepsilon), \ \cos\theta-\cos(\theta+\delta))$$

$$\fallingdotseq\mu(2\sin\theta\cos\varphi+\delta\cos\theta\cos\varphi+\varepsilon\sin\theta\sin\varphi, \ 2\sin\theta\sin\varphi+\delta\cos\theta\sin\varphi-\varepsilon\sin\theta\cos\varphi, \ \delta\sin\theta). \quad (4)$$

In eq 4 and hereafter the subscripts of angular variables for the monomer 1 were omitted ($\theta_1\rightarrow\theta$, $\varphi_1\rightarrow\varphi$). The dipole instantaneously induced with atomic motions in the dimer do not cause a dielectric relaxation. The average of the dipole moment of eq 4 should be non-zero to cause the dielectric relaxation. A dielectric relaxation is observed only when the life span of dipole is sufficiently long in comparison with the time scale of the atomic motion. A dielectric relaxation can be caused by the dipole of which life is longer than at least $10^{-1}-10^{-2}$ times the relaxation time. The average of dipole moment for one dimer can be calculated on the assumption that δ and ε are constant for the time interval to take an average. The average m of a dipole is

$$m_{x,y,z}=\langle\mu_1+\mu_2\rangle_{x,y,z}$$

$$= \left\{\int_{-\pi}^{\pi}d\varphi\int_{0}^{\pi}\exp(-U/k_BT)(\mu_1+\mu_2)_{x,y,z}\sin\theta d\theta\right\}/\left\{\int_{-\pi}^{\pi}d\varphi\int_{0}^{\pi}\exp(-U/k_BT)\sin\theta d\theta\right\}, \quad (5)$$

where k_B is the Boltzman constant, T temperature, and U the potential for the angular motion of the dipole. The potential U is assumed to be given in terms of the sum of the harmonic potential of bending and the periodic one of the rotation:

$$U = \frac{A\theta^2}{2} + \frac{1+\cos(2\varphi)}{2}V_0, \tag{6}$$

where A denotes the force constant of bending motion for the dipole and V_0 a barrier of rotation. It is easily proved that the x and y component of a dipole are zero in the evaluation of eq 5 with the potential of eq 6. Thus the average value of a dipole is given as

$$m_x = 0, \qquad m_y = 0, \qquad m_z = \mu\delta B$$

where

$$B = \left\{ \int_{-\pi}^{\pi} d\varphi \int_0^{\pi} \exp(-U/k_BT)\sin^2\theta d\theta \right\} / \left\{ \int_{-\pi}^{\pi} d\varphi \int_0^{\pi} \exp(-U/k_BT)\sin\theta d\theta \right\}$$

$$= \left\{ \int_0^{\pi} \exp(-A\theta^2/2k_BT)\sin^2\theta d\theta \right\} / \left\{ \int_0^{\pi} \exp(-A\theta^2/2k_BT)\sin\theta d\theta \right\}. \tag{7}$$

The value of B was numerically calculated as shown in Table I . The B value was found to depend on $A/2k_BT$ in some extent, but not on the barrier V_0 of rotational potential and the phase shift ε. The dipole of the dimer unit results from the difference between two monomer dipoles. The components perpendicular to the z axis are averaged out to zero because of the speedy motions of there components. The dipole is oriented in the direction of the z axis. The dipole moment is proportional to the phase shift δ, which specifies the monomeric character and the disturbance strength. It is easily shown that the dipole of the dimer is caused by the non-alternation of signs of the phase shift δ for averaging, where the assumption of the constant phase shift is not necessarily required. The life of the dipole is considered to be the period for the non-alternation of signs of δ. The direction of the dipole is constant and the magnitude of the dipole as well as δ changes with time.

We define the space-fixed coordinates as a parallel shift of the molecule-fixed. The direction of the dipole in laboratory frame has an advantage to observe the dielectric relaxation, since the crystalline c-axis which is the approximate

direction of the dipole seem to be nearly parallel to the electric field considering the strong (00l) X-ray reflections. The electric field crosses the dipole at a small angle. The calculated moments of dimer units distribute according to the distribution of δ. We assume that the probabilities P_δ, where the phase shift for one dimer is δ, is given by the Gaussian distribution as,

$$P_\delta = 1/(\ (2\pi)^{1/2}\delta_0)\exp(\ -\ \delta^2/2\delta_0^2\ ), \tag{8}$$

where δ_0 is the standard deviation of δ. The average $|m|$ of the dipole moment is estimated for an ensemble of dimers as

$$|m| = (2/\pi)^{1/2}\mu\delta_0 B. \tag{9}$$

In this model δ_0 as well as the dipole moment $|m|$ of the dimer increase with temperature, while the dipole moment μ of a monomer and B are almost independent of temperature change. The calculated temperature dependence of the dipole moment agrees qualitatively with the experimental results. In Figures 1-3 the location of loss maximum shifts to higher frequencies with temperature, suggesting that the life of the dipole is shorter at higher temperatures.

Now we roughly estimate the dipole moment of this model. Since the bond moment for OH or O$\cdots$H is dominant for the dipole of a dimer, the force constant A of bending motion for the dipole (see eq 6) can be approximated by coefficient $kr_{OH}r_{O\ldots H}$ of the OH out-of-plane bending motion. The force constant k was given by Umemura[19] as 0.042 mdynÅ^{-1}rad^{-2} and the distance r_{OH} and $r_{O\ldots H}$ are 1.0 and 1.64 Å , respectively.[20] The temperature where the dielectric relaxation was observed is about 200 K and the value of $A/2k_BT$ is about 12.5 so that B=0.244. To estimate the phase shift δ_0, the probable bending angle θ was estimated to be 0.3 radian from the relation: $kr_{OH}r_{O\ldots H}\theta^2/2k_BT = 1$. Thus δ_0 is 0.3 radian at most and the actual phase shift is probably about δ_0 = 0.1 radian. The value of 1.74 D for the dipole moment μ of the monomer unit is adopted from the data for the stearic acid in dioxane solution.[21] Then the average moment is calculated as $|m|$ =0.034 D. We compare the estimated dipole moment with the experimental one in Table I, though

this dipole was calculated on the proposed model while the experimental one by Onsager's equation. The agreement of these two values is reasonable. As discussed above, the centrosymmetric dimer can have a dipole. The vector sum law holds only in the short time interval but not in the averaged dipole.

Difference of Odd from Even Numbered Acids. The dielectric relaxations caused by the dipole were observed in the low temperature phase of odd numbered acids, while not in the high temperature phase C' of odd numbered acids and not in the even numbered acids. The dipole moment discussed in the preceding paragraph is determined by a single parameter δ defining the phase shift. The large phase shift yields the dipole large enough to detect. The small phase shift yields the dipole too small to detect in the even numbered acids and in the high temperature phase of odd numbered acids. The dipole moment observed in the low temperature phase of odd numbered acids is due to the weak monomer-monomer interaction(i.e. a large phase shift). The monomer-monomer interaction in the dimer unit can be a sole function of the strength of hydrogen bond. The strength of hydrogen bond has been investigated by many infra-red studies. The OH out-of-plane bending motion at 80 K locates at[22] 960-980 cm^{-1} for even numbered acids and the super-cooled C'-form of undecanoic acid while at[23] about 885 cm^{-1} for the odd numbered acids of low temperature phase (B' for undecanoic and pentadecanoic acids and A' for tridecanoic acid). The wavenumbers for the odd numbered acids are about 90 cm^{-1} lower than those for the even numbered acids. These low wavenumbers suggest[24] that the hydrogen bond in the low temperature phase of the odd numbered acid is weaker than that of even numbered acid. The crystal field and the interaction with neighboring dimer affect the strength of the hydrogen bond and the phase shift. The dimer of weak hydrogen bond yields the independent motion of the individual monomers. The field which weakens the hydrogen bond gives a large phase shift. The phase shift δ in the low temperature crystalline phase of odd numbered acids are large enough to observe the

dielectric relaxation whereas not in the even numbered acids. The large difference in imaginary parts of permittivity for pentadecanoic acid from undecanoic and tridecanoic acids is the object for future studies.

The thermal hysteresis loops seen in Figures 4-9 suggest that the cooling or heating rate are too fast to observe the equilibrium permittivity. The dispersion of the Curie-von Schweidler law observed around 300 K for six compounds may be caused by space charge effects but is not discussed here, because this dispersion has no relation with the dielectric relaxation in question.

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TABLE I: Relaxation intensities and the dipole moment of fatty acid dimer on the assumption of the Onsager fields. The densities of acids were taken as 1 gcm^{-3} in accordance with the Sydow's value[15] of 1.02 of undecanoic acid at 23 °C.

undecanoic acid			tridecanoic acid		
temp./K	$\Delta\varepsilon/10^{-3}$	μ/D.	temp./K	$\Delta\varepsilon/10^{-3}$	μ/D.
202.1	11	0.15	147	2.8	0.07
208.5	12	0.16	160	3.9	0.08
212.4	12	0.16	177	5.2	0.10
216.9	13	0.17	190	5.9	0.11

TABLE II: B value for several potential parameter.

$A/2k_BT$	7.5	10	12.5	15	17.5	20	25
B	0.310	0.271	0.244	0.224	0.208	0.195	0.175

Figure captions

Figure 1. Imaginary parts of relative permittivities for the B'-form of undecanoic acid against frequency. The temperature maintained is indicated in the figure. The difference between cooling and heating processes was not observed within an experimental error. The measurements were carried out with the Ando TR-10 transformer bridge.

Figure 2. The same as in Figure 1 for the A'-form of tridecanoic acid.

Figure 3. The same as in Figure 1 for the B'-form of pentadecanoic acid. The measurements were carried out with the GR-1616 transformer bridge. The loss maximum for the relaxation was indicated by the arrow.

Figure 4. Real parts of relative permittivities for the B'- and C'-form undecanoic acid against temperature. The process of cooling or heating and the frequency are denoted in the figure.

Figure 5. The same as in Figure 4 for the A'- and C'-form of tridecanoic acid.

Figure 6. The same as in Figure 4 for the B'- and C'-form of pentadecanoic acid.

Figure 7. The same as in Figure 4 for the C-form of lauric acid.

Figure 8. The same as in Figure 4 for the C-form of myristic acid.

Figure 9. The same as in Figure 4 for the C-form of palmitic acid.

Figure 10. The dipole direction at an instant in the molecule(dimer)-fixed coordinates. Capital letters of C, H, and O denote the average positions of atoms. The large size letter means forward the plane of the paper and the small size behind. All carbon and oxygen atoms are in the x-z plane on the average. The space-fixed coordinates are the parallel shift of the molecule-fixed. The z-axis denoted with dotted broken line is parallel to the averaged direction of the monomer dipole and a broken line is parallel to the c-axis in crystal.