

Light-scattering study on the shear-orientation coupling of liquids near isotropic-to-nematic phase transition

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(Received 26 June 2005; revised manuscript received 6 September 2005; published 20 October 2005)

Microscopic interaction between the translation and rotation of rodlike molecules yields the shear-orientation coupling in the macroscopic view. The depolarized scattering component arising from orientational fluctuations gives a constant in the strength of the coupling, which is related to the three viscosity parameters introduced by de Gennes. A high-resolution system of light scattering with an improved optical beating method was utilized for measurements in the 4-cyano-4'-alkylbiphenyl (*n*CB) series: propyl (3CB), butyl (4CB), pentyl (5CB), hexyl (6CB), heptyl (7CB), and octyl (8CB). All the coupling constants obtained in these samples showed clear dependence on temperature, and their behaviors were interpreted in terms of a critical phenomenon near T^* , the virtual isotropic-nematic phase transition point. The values of T^* were also given by the light scattering experiment, and the critical exponent of shear-orientation coupling was determined to be 0.31. Furthermore, the characteristic value of the coupling constant was correlated with the aspect ratio of these rodlike molecules, and two clear facts were found: a stronger coupling in longer molecules; and an odd-even effect with respect to the number of C-C bonds in the alkyl chain.

DOI: [10.1103/PhysRevE.72.041707](https://doi.org/10.1103/PhysRevE.72.041707)

PACS number(s): 64.70.Md, 66.20.+d, 42.68.Mj, 64.60.Fr

I. INTRODUCTION

Different degrees of freedom in molecular motions interact with each other in some soft condensed materials, and the coupling therein may be the origin of somewhat extraordinary phenomena that can be applied to new functional materials. A typical example is the flow induced or forced phase transition [1,2] caused by the interaction between the molecular translation and rotation. A steady shear flow assists molecules in organizing a highly ordered structure with anisotropy as seen in liquid crystals or the lamellar structures of biotissues. Although many studies have been made to observe the translation-rotation coupling in the liquid state, few of them have given a quantitative analysis that would help us to envisage whether the coupling for a molecule under study is strong or weak. Therefore we carried out an experimental study to directly observe the coupling constant, which is the best measure of efficiency for the energy transfer and/or dissipation occurring between the different degrees of freedom. This complex dynamics reveals itself most explicitly at the critical stage of a phase transition. The purpose of this study is to clarify how a transition phenomenon is affected by the shear-orientation coupling, and which property of the molecules determines the coupling strength.

The phenomenological formula introduced by de Gennes describes the system with a degree of freedom represented by the local orientational order [3]. He modified classical hydrodynamics equations by adding the cross terms that connect the translational and orientational motions. This formula includes three kinds of viscous coefficient η , ν , and μ , of which η is the shear viscosity commonly known as the transport coefficient of the translational momentum; ν is the rotational viscosity associated with the diffusing process of the

rotational momentum; and μ is the coupling viscosity representing the energy conversion between the two modes. This study deals only with the isotropic phase, and each of these viscosities is treated as a scalar even in the vicinity of the phase transition to anisotropic liquid crystals.

While the value of η has been measured and its temperature dependence is also known in detail for the liquids of our interest, reliable values of ν or μ are not available due perhaps to the absence of techniques for directly observing them. Nevertheless, measurements of the shear-orientation coupling have been proposed and actually made to estimate a constant giving the ratio of η , ν , or μ . One is the flow birefringence method [4,5], in which one applies a shear strain to fluids with a steady flow or ultrasonic waves, and observes the induced birefringence with an optical technique: a coupling constant defined by $C' \equiv \mu/\nu$ is obtained. Unfortunately, the ultrasonic technique does not provide us with an absolute value because of the difficulty in exact estimation of the shear strain. As for the steady flow method, on the other hand, the range of the applied shear rate is technically limited and restricts observation of the fast dynamics. Another method, and a more sophisticated one, is to detect the depolarized component in the dynamic light scattering [6]. Thermal energy drives orientational fluctuations, and the local inhomogeneity in the dielectricity causes the light scattering. The coupling constant $C \equiv 2\mu^2/\eta\nu$ is an independent parameter appearing in the optical spectrum of the depolarized scattered component. There is a great advantage of this method over the former in that the absolute value of C is readily given. All we need is to obtain a precise spectrum with high-frequency resolution. Further, we can observe the raw process of the phase transition without adding any external forces such as artificial flow or ultrasonic waves. Therefore we decided to conduct a light scattering measurement and observe C in this study.

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II. THE SHEAR-ORIENTATION COUPLING IN THERMAL FLUCTUATIONS

A local orientational order deriving from thermal fluctuations spontaneously arises and vanishes in isotropic liquids consisting of anisotropic molecules. The light passing through this medium and scattered by the fluctuations suffers from rotation in the polarization plane. We chose two typical scattering modes in the experiment, referred to as VV and VH. Here V and H imply the vertical and the horizontal polarization, respectively, with respect to the scattering plane determined by the wave-number vectors of the incident and scattered light. We fixed the incident polarization to V in the experiment, and selectively detected the scattered component polarized to V or H corresponding to VV or VH modes, respectively.

The VV component comes from the diagonal factors of the dielectric tensor that describes the fluctuation, and therefore reflects only the rotational motion independent of the coupling with local shear flows. The VV scattering shows the spectrum of the Lorentzian shape for a single relaxation process. It is written as

$$I_{VV}(q, \omega) = \frac{2\Gamma}{\omega^2 + \Gamma^2}, \quad (1)$$

where q is the scattering wave number (or wave number of the observed fluctuation), ω is the angular frequency, and Γ is the orientational relaxation frequency determined as the half width at half height of the peak. Note that a Brillouin triplet of the ordinary sense (the Rayleigh and the two phonon peaks) should be superimposed on this spectrum, though ignored here.

On the other hand, more interesting for us is the VH component that provides us with information on the shear-orientation coupling. The depolarized scattered light shows a spectrum of an extraordinary shape with a central dip. The spectral curve is written as [3,7]

$$I_{VH}(q, \omega) = \frac{2\Gamma}{\omega^2 + \Gamma^2} \sin^2 \frac{\theta}{2} + \frac{2\Gamma[\omega^2 + \gamma^2(1 - C)]}{(\omega^2 - \gamma\Gamma)^2 + \omega^2[\Gamma + \gamma(1 - C)]^2} \cos^2 \frac{\theta}{2}, \quad (2)$$

where θ is the geometrical scattering angle, and $\gamma \equiv \eta q^2 / \rho$ is a characteristic frequency inversely proportional to the decay time of the shear flow, with ρ being the density. While the first term is of the same shape as the VV spectrum given by Eq. (1), the second has a dip at the center and the width of this dip is approximately given by γ .

We utilized optical beating spectroscopy in the present study. The extraordinarily high resolution allowed us a small scattering angle ($\theta \ll 1$): the contribution of the first term decreases as $\sin^2 \theta$. Furthermore, we chose the scattering angle so that the condition $\Gamma / \gamma \gg 1$ holds. Then the second term in Eq. (2) can be approximated to

$$I_{VH}(q, \omega) \approx \frac{2\Gamma}{\omega^2 + \Gamma^2} - C \frac{\gamma}{\Gamma} \frac{2\gamma}{\omega^2 + \gamma^2}. \quad (3)$$

This spectrum has the shape of a Lorentzian curve with another Lorentzian peak subtracted: the former represents the independent rotational relaxation appearing in the VV scattering; and the latter is associated with the dissipation via a coupled shear flow. It is easily perceived that the ratio of the second term to the first (the depth of the inner dip to the outer spectral height) directly gives the coupling constant C .

Spontaneous orientational fluctuations generate shear flows and the excess flow momentum is paid back to the rotational motion but in the inverse phase. Of course fluctuations of the spontaneous origin can happen on the side of the shear flow with the same probability. Thus, the two degrees of freedom exchange momentum with each other through shear-orientation coupling. Since thermal energy as a driving force evenly works on both modes, we obtain the coupling constant in the form of $C = 2\mu^2 / \eta\nu$ in this light scattering method: C includes all three viscosity coefficients.

In the experiments of VH scattering made so far, the Fabry-Pérot interferometer has been the standard equipment for analyzing the spectrum. The measurements of C have been conducted for some liquids including anisaldehyde [7], triphenyl phosphate [8], ethyl benzoate [9], and so on [10,11]. All the results show that C has values from 0.28 to 0.45 and has little dependence on temperature over the range 30 to 50 °C. These molecules have very fast rotational relaxation, Γ ranging over the gigahertz region. The frequency resolution of the Fabry-Pérot interferometer is ca. 1 GHz. In order to observe the narrow dip around the center with limited resolving power of the spectrometer, they must have chosen a large value of q , and hence θ has been commonly set at 90°. Then the first term of no concern to the coupling in Eq. (2) has a comparable contribution to the spectrum as the second term of greater significance. Therefore no quantitative relation has been found yet, though it is supposed that the anisotropy in the molecular shape directly rules the coupling constant [6].

We have a particular interest in the phenomenon in the vicinity of the isotropic-to-nematic transition, in which the cooperative orientational order increases its correlation length divergently toward the transition point; and hence the time scale of the fluctuation increases infinitely. Within the framework of mean-field theory, this critical slowing down is given by the following power law [3]:

$$\Gamma = \frac{a(T - T^*)^{1.0}}{\nu}, \quad (4)$$

where T^* is the virtual critical point of the continuous second-order phase transition, and a is a constant independent of temperature. This relation has been verified by a previous light scattering experiment [12]. A measurement in the region of critical slowing down requires very high resolution to reproduce the fine spectral shape: even the outer peak given by the first term of Eq. (3) is narrower than 10 MHz. Such high resolution can be available only with the optical beating spectroscopy. This technique has been successfully used in spectroscopy for ripplon light scattering

[13] and Rayleigh-Brillouin experiments [14,15]. Furthermore, accurate spectra near the isotropic-to-nematic phase transition have been obtained [16] and the possibility of C depending on temperature have been shown [17].

In the present study, we made effective improvements to the experimental system and increased the sensitivity as well as the available frequency range. We studied the coupling phenomenon on decreasing the temperature from 70 °C down to the point just before the phase transition occurs (from the normal liquid state down to the pseudonematic liquid in the pretransition region) and precisely investigated the temperature dependence. We found a clear critical behavior in C for the homologous series of cyanobiphenyles (n CB, with $n=3-8$). The relation between the length of the alkyl chain and the coupling constant is also discussed.

III. EXPERIMENT

A. Samples

Molecules in the n CB group are compounds with a rod-like structure that is apt to be involved in the complex coupling of our interest, and arrange themselves into an ordered state. We chose them as the samples of this study since we aimed to clarify how the molecular anisotropy affects the coupling dynamics. The anisotropy is described simply by the aspect ratio in dimension, and samples with different molecular length are readily available in a series in the same group. Additionally, they are chemically tough against light exposure and moisture in the atmosphere. All the samples were purchased from Merck and used without further purification. Each of them was poured into a glass cell kept in a water jacket for controlling temperature within the accuracy of 0.1 °C.

Cooled down gradually in the isotropic phase, they undergo the transition to the nematic phase at a certain temperature T_{IN} , about 1 °C above T^* . In 3CB and 4CB, however, it is known that they change directly to the solid phase at the melting point without going through the liquid crystal phase. It is also interesting to know whether or not these two species show different behaviors from the others.

B. Optical beating system

The light source is a cw-mode yttrium aluminum garnet laser emitting 5 W power at 532 nm (Coherent Verdi). The output beam is divided with a beam sampler into two paths: a very intensive light used for the incidence, and a weak one for the reference for optical beating. The scattered and the reference lights are superposed on each other and mixed by an avalanche-type photodiode (Hamamatsu Photonics s9074), which gives the beating signal in the output current. The spectrum analyzer combined with other electronic equipment achieved a very accurate and precise spectroscopy with frequency resolution better than 10 kHz [15]. We could readily alternate the VV and VH scattering by rotating a half-wavelength plate put into the reference path. We used an acousto-optic modulator to shift up the frequency of the reference light by 110 MHz so that we could avoid serious electric noise appearing around zero frequency of the spec-

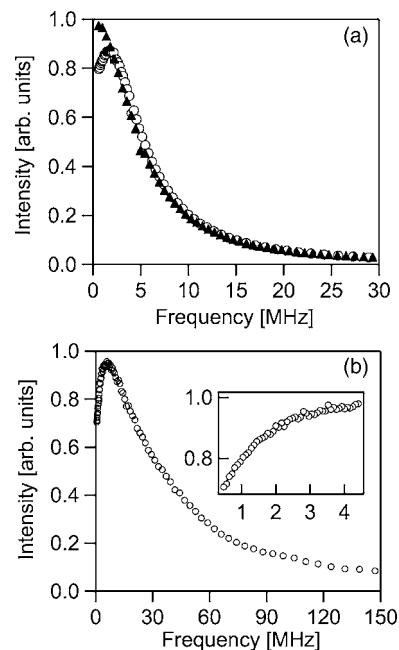


FIG. 1. Typical spectra for (a) 8CB observed at 48.9 °C and (b) 3CB at 61.3 °C. The triangles and the circles in both figures denote the VV and VH spectra, respectively. The inset in the lower figure shows the dip part in a magnified scale.

trum analyzer. The scattering angle was set at 2°–5°, small enough to satisfy the condition required for the approximation of Eq. (3).

The independent parameters appearing in the VV and VH spectra are Γ , γ , and C . They were determined in the following procedure. First, we used VV scattering and decided Γ from the observed VV curve in the fitting of Eq. (1). This equation includes only Γ as an adjustable parameter and gives a very accurate value at each temperature. Second, we rotated the polarization of the reference beam for the VH scattering, keeping all the other experimental conditions. With Γ having been fixed, Eq. (3) for the VH curve has only two unknown parameters γ and C , of which γ is determined with little ambiguity since it is much smaller than Γ in the small scattering angle of this experiment even at temperatures near T_{IN} . Note that Γ and γ are the widths of the outer peak and the inner dip, respectively. Finally, the reliable value of C and its temperature dependence were determined. Furthermore, the dependence of Γ on temperature thus obtained yielded the virtual phase transition temperature T^* , another very important factor characterizing the critical behavior.

Typical examples of the VV and VH spectra obtained at about 9 °C above T^* are shown by the triangles and the circles, respectively, in Fig. 1(a). The VH curve clearly has the central dip expressed by the second term in Eq. (3). The lower figure shows the VH spectrum for 3CB at a temperature about 40 °C higher than the expected value of T^* , and the inset figure gives the detail of the dip part on magnified axes.

IV. RESULTS AND DISCUSSIONS

Figure 2 shows the temperature dependence of the orientational relaxation frequency Γ for 5CB, 6CB, 7CB, and

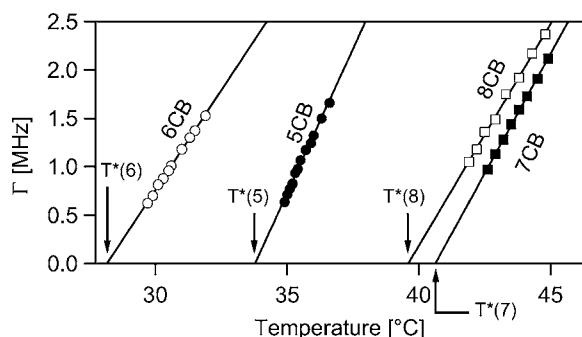


FIG. 2. Temperature dependence of the orientational relaxation frequencies Γ for 5CB (●), 6CB (○), 7CB (■), and 8CB (□). Extrapolating the fitted line onto the temperature axis, we determined the vertical transition temperature T^* .

8CB. The data obtained in the temperature region close to the isotropic-to-nematic phase transition were exhibited. All the points show a good linear dependence on temperature as suggested by Eq. (4), and T^* was determined as the intercept of the fitted straight line on the horizontal axis. The virtual critical point is thus determined within ambiguity of ± 0.5 °C and listed in Table I. We conducted the experiment for the supercooled state of 3CB and 4CB below the melting point, in anticipation of finding T^* in these liquids that have no substantial nematic phase. It was impossible, however, to keep the metastable state down to the temperatures at which Eq. (4) for the critical slowing down holds well. Instead, the literature values [18] shown in the table were used as T^* in analysis of the critical behavior given later.

A. Criticality in C

The values of C determined for all six n CBs, n being 3–8, are plotted versus temperature in Fig. 3. It was verified that the coupling constant has a dependence on temperature and, most interestingly, all the curves for different molecules seem to exhibit a decrease toward T^* of each molecule, which suggests a possibility of the critical behavior in C . As has been the common scheme in analysis of critical phenomena, we introduce here the reduced temperature ε defined by $\varepsilon \equiv (T - T^*)/T^*$ with T^* shown in Table I. Further, we assumed a critical exponent α that characterizes the near-transition behavior of C in the following form:

$$C = C_0 \varepsilon^\alpha, \quad (5)$$

where C_0 is a constant independent of temperature. The inset figure of Fig. 3 shows the logarithmic plot of C against the

TABLE I. Characteristic values determined and used in this study. Numbers in parentheses denote the literature value.

Sample	T^* (°C)	Critical exponent (α)	C_0	C_{liq}
3CB	(24.5)	0.312	0.615	0.310
4CB	(15.5)	0.310	0.589	0.298
5CB	33.8	0.310	0.678	0.343
6CB	28.2	0.316	0.652	0.326
7CB	40.5	0.306	0.748	0.382
8CB	39.5	0.305	0.750	0.384

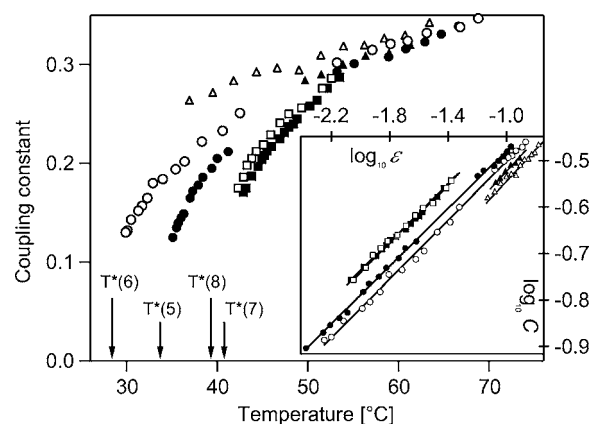


FIG. 3. Temperature dependence of C for all the cyanobiphenyl specimens 3CB (▲), 4CB (△), 5CB (●), 6CB (○), 7CB (■), and 8CB (□) in the liquid state. The arrows indicate the virtual transition points T^* for the specimens with number (n). The inset is the logarithmic plot, which shows the critical behavior toward T^* .

reduced temperature ε . We find that all the points for each molecule are very well fitted with a straight line and that the gradient is almost independent of the molecules. These two facts strongly support the hypothesis of criticality expressed by Eq. (5).

The critical exponents α were determined as the slope of these lines and listed in Table I together with the fitted values of C_0 . We determined $\alpha = 0.31$ as the average value of all the specimens, taking the tolerance in the fitting procedure into account. We expect that this critical exponent is a universal constant common not only to the species with isotropic-to-nematic phase transitions but also to other rodlike molecules that have no real phase transition. Equation (5) describes the dynamics in which the molecular interaction between the neighbors and all around leads to the efficient and optimum packing of molecules against thermal stirring. This hypothesis should be inspected by studies on liquids of other kinds than the homologous cyanobiphenyl series, though a theoretical prediction on α is absent at present.

The origin of criticality in the coupling constant should be attributed to any of η , ν , or μ . It is well known that the shear viscosity η shows no anomalous behavior near T^* . Little dependence of ν on temperature near T^* is clearly indicated by Eq. (4) together with the experimental fact that Γ increases with $(T - T^*)^{1.0}$. Then the observed criticality in C is entirely due to μ , and $\alpha = 0.31$ suggests the critical exponent of 0.15 for μ since C is proportional to μ^2 .

The coupling constant is defined by μ which is a macroscopic and somewhat phenomenological viscosity parameter for the cooperative motion of many molecules. Nonetheless, the elementary process of momentum transfer is a single molecular motion: a rotation around the shorter axis of the rodlike molecule can drive its neighbor into lateral motion of the center of gravity, and vice versa. This would be the simplest picture describing the origin of μ , and is quite convincing at high temperature where the molecules are freely rotating, governed by thermal energy. As temperature decreases toward T^* , the energy-saving effect of the close packing surpasses the entropic effect of random disorder, and the mo-

molecular rotation is restricted in the interaction with neighbors. Then the rotation is isolated from the translation and C disappears at $T=T^*$ as described by Eq. (5), though the whole system changes to the nematic phase at $T=T_{IN}$ ($T_{IN} > T^*$) due to the effect of the third- and fourth-order terms of the free energy expansion with respect to the local-order parameter. The coupling constant is thus a negative and suppressing factor for the nematic phase, yet the most important parameter controlling the isotropic-to-nematic phase transition.

B. Molecular shape and C

If the above consideration is correct and a single-molecular rotation is the origin of μ , it would be worthwhile to correlate C with the aspect ratio of the molecular shape, expecting a larger C value for a longer one. Assuming a spheroid shape of the molecule, we defined the aspect ratio r as the ratio of the longer axis to the shorter ($r=l_b/l_a$), where l_a and l_b are determined by the bonding length and the van der Waals radii of atoms under the condition that C-C bond is a free-rotating axis. Note that $r=1$ means a molecule of the spherical shape. We fixed the same value $l_a=0.67$ nm for all the specimens as the thickness of phenyl group, and got $l_b=1.68, 1.76, 1.89, 1.97, 2.09,$ and 2.17 nm for 3CB, 4CB, 5CB, 6CB, 7CB, and 8CB, respectively. An addition of alkyl chain from $n-1$ to n increases l_b by 0.12 and 0.08 nm when n is odd and even, respectively, since the bonding of the odd chain is on the axis of biphenyl group while the even chain is off the axis by 109° .

Note that C_0 corresponds to C at $T=2T^*$ (~ 600 K), impractical temperature for liquids. Then we introduced another characteristic coupling constant C_{liq} . According to the Landau-de Gennes theory, the correlation length of the local orientational order increases toward T^* as $\xi=\xi_0\epsilon^{-1/2}$. It was found that this relation breaks above a certain temperature at which the length of the pseudonematic domain is equal to three molecular lengths ($\xi=3\xi_0$) [19]. Substituting $\epsilon^{-1/2}=3$, i.e., $\epsilon=1/9$, and the determined values of C_0 and α into Eq. (5), we calculated C_{liq} as the appropriate value for each specimen in the normal liquid state.

Figure 4 shows C_{liq} versus r plotted for the six specimens. A marked feature of this figure is the clear odd-even effect, in which the change with respect to n takes a regular up-and-down curve and the species with odd-number alkyl chains have higher values than the neighboring two with even n .

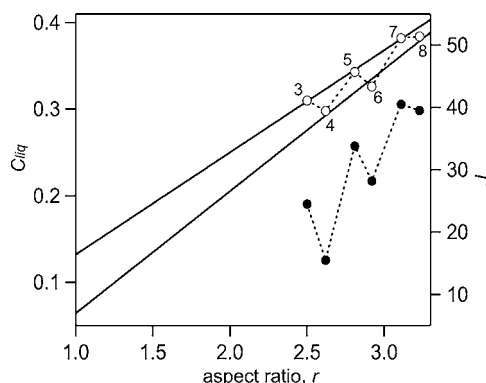


FIG. 4. Dependence of C_{liq} (open circles) and T^* (closed circles) on the aspect ratio. Clear odd-even effect is observed in both of them. The solid lines are fitted to the points of the odd and even groups.

This kind of odd-even effect is generally found in various physical properties including T_{IN} and the melting point of molecules with alkyl chains. In fact T^* indicated by the closed circles in Fig. 4 has a trace very similar to C_{liq} . It would be natural that values for the odd and the even approach each other as n increases: the odd-even effect disappears for very long alkyl chains.

When we pick up only the points of even numbers, for example, they are well on a straight line with a positive slope, and the extrapolation goes to $C_{liq}=0.06$ at $r=1$, close to 0. This result is in quantitative agreement with our anticipation that a longer molecule should have a larger C value, and $C_{liq}=0$ for a spherical one. The straight line for the odd group is against our anticipation, however, and strikes the axis at $C_{liq}=0.13$. Our model of a spheroid is the simplest one that identifies the molecule only by its aspect ratio without any distinction for odd or even. Figure 4 obviously suggests that a finer model for the molecular shape is required. Taking the feature of odd and even into account, we are ready to propose a more sophisticated model though a quantitative analysis is not yet successful.

ACKNOWLEDGMENT

This work was partially supported by a Grant-in-Aid from the Ministry of Education, Culture, Sports, Science and Technology.

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