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Ultrafast solvation dynamics: Molecular explanation of computer simulation results in a simple dipolar solvent

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Recently Perera and Berkowitz [J. Chem Phys. **96**, 3092 (1992)] and Neria and Nitzan [J. Chem. Phys. **96**, 5433 (1992)] carried out computer simulations of solvation dynamics of an ion in dense Stockmayer liquids. Both the simulations observed an ultrafast component which decays in a few tens of femtoseconds with a Gaussian time dependence. This is followed by a slow exponential-like decay with a time constant of a few picoseconds. It is shown here that many of the simulation results can be explained very well from a first principles theory with no adjustable parameter.

I. INTRODUCTION

Ultrafast solvation in dipolar liquids is a subject of much current interest. Computer simulations,[1] experiments,[2] and theoretical studies[3] have all indicated that the solvation of an ion in an underdamped liquid is *biphasic* with the phases showing very different dynamic characteristics. The solvation of the ion starts with an ultrafast component which decays in a few tens of femtoseconds with a Gaussian time dependence. This component contributes about 60%–80% to the total relaxation. This is followed by a slow, exponential-like decay with a time constant in the picosecond domain and this carries the rest of the strength. Computer simulations[1] and theoretical studies[3] also indicated that this slow long time decay may arise from diffusive relaxation processes involving primarily the first nearest-neighbor molecules of the solute ion. On the other hand, it is the nature of the initial Gaussian decay that is not clear yet. Two rather different explanations have been put forward. It has been suggested[3] that this Gaussian decay can arise from an underdamped orientational relaxation in a macroscopic polarization potential. Since this potential originates from many-body interactions, it may be fair to call the relevant motion as a collective excitation, like a libration (or, even a dipolaron). On the other hand, Cho *et al.*[4] has made the interesting suggestion that the Gaussian decay could be explained in terms of the unphasing of independent polarization oscillators. These two interpretations are fundamentally different. Clearly, computer simulations in simple model systems can play an important role in clarifying the nature of the initial decay.

Two recent molecular dynamics simulations[5,6] in Stockmayer liquid (which consists of Lennard-Jones spheres with point dipoles at their centers) can serve precisely this purpose. These simulations have provided us with a large amount of quantitative information which might help in resolving the nature of the initial decay. In agreement with earlier studies, it was observed that the solvation was dominated by an inertial component which contributed about 80% of the total solvation energy. This inertial decay could be fitted to a Gaussian form $\exp[-(t/\tau_G)^2]$ with τ_G very small, sometimes even less than 200 fs. If one defines a parameter $p=I/M\sigma^2$, where M, I, and σ here are the mass, the moment of inertia and the diameter of the solvent molecules, p can be a measure of the importance of the translational modes in the solvent polarization relaxation. Both Perera and Bekowitz[5] and Neria and Nitzan[6] have investigated the effect of p on solvation dynamics. Neria and Nitzan varied p by varying I except in one case where p was set to zero by making the molecules infinitely massive. An interesting observation was that the dependence of the inertial decay time τ_G on I was *considerably weaker* than the free rotor model[7] which predicts that τ_G should be proportional to $I^{1/2}$. As mentioned earlier, the nature and the origin of this inertial decay is not fully understood yet. It was also observed that the slow long time decay component which came primarily from the first shell was quite sensitive to the translational modes which is in agreement with theoretical studies.[3] The results of these two simulations[5,6] are rather similar, although it is somewhat easier to calculate the solvation dynamics for the system of Neria and Nitzan[6] because it is less polar of the two.

The short time dynamics in a Stockmayer liquid is expected to be much simpler than that in liquid water or acetonitrile because of the simplicity of the model potential and also because the system is purely classical and molecules are nonpolarizable. The solvation dynamics is further simplified because the solute in these simulations is a sphere of almost the same size as the solvent molecules (so the solvent is not severely perturbed) with a point charge at the center. Therefore, a reliable microscopic analysis of these results can be performed. A further motivation for a theoretical analysis of the initial decay is provided by the observation that the short time dynamics in a classical monatomic liquid is well understood and extensions of the

analogous concepts to treat the rotational motion can be performed rather easily. This is to be contrasted with the earlier theoretical analysis[3] where approximations were necessary for the viscoelastic properties of the solvent. In this article we present a theoretical analysis of the computer simulation results[5,6] by using the same microscopic theory used before and described in detail elsewhere,[3] but without any serious approximation. The implementation of the theory requires knowledge of the orientational structure factors of the dipolar liquid and of the frequency dependent rotational and translational frictions. Because of the simplicity of the model system, we can calculate these quantities fairly accurately. One important simplification is that *dielectric friction is the only source of rotational friction in the Stockmayer fluid* and fortunately, the short time behavior of this friction can be determined fairly accurately. A key role in the present development is played by the orientational Einstein frequency which is defined as the second moment of the lineshape function (which is the Fourier transform of the angular velocity correlation function).[8] The latter quantity is also defined as the mean square torque on a tagged molecule.[8] We refer to several recent papers[9] for detailed discussions of the translational analog of this quantity.

The organization of the rest of the paper is as follows. In Sec. II, we discuss the main theoretical points. In Sec. III, we present the numerical results. Section IV concludes with a discussion.

II. THEORETICAL DISCUSSIONS

We shall now try to reproduce the essential aspects of the short time dynamics observed in the computer simulations. Since the theory has been discussed in detail elsewhere,[3] we shall concentrate on the evaluation of the short time frictions and the results. For simplicity we shall first neglect the translational motion of the solvent molecules (as was done in one of the simulations of Neria and Nitzan[6]) and consider only the long wavelength polarization fluctuation as it is the *fastest mode* that contributes to solvation dynamics. We expect this mode to make a significant contribution to the ultrafast solvation dynamics of an ion.[3] In this limit, the solvation time correlation function, $S(t)$, is given by the following relation:

$$S(t) = \frac{E_{\text{solv}}(t) - E_{\text{solv}}(\infty)}{E_{\text{solv}}(0) - E_{\text{solv}}(\infty)} = \frac{P_{\text{LL}}(t)}{P_{\text{LL}}(0)}, \quad (1)$$

where $E_{\text{solv}}(t)$ is the solvation energy of the ion at time t and $P_{\text{LL}}(t)$ is the long wavelength (macroscopic) longitudinal polarization fluctuation at time t. We show that in this limit the theory is transparent—the full calculation is discussed later in this paper. The equation of motion for the long wavelength longitudinal polarization fluctuation is given by

$$\frac{d^2}{dt^2} P_{\text{LL}}(t) = - \int_0^t dt' \zeta_R(t-t') \frac{dP_L}{dt'}(t')$$
$$- \frac{2k_B T}{I} f_L^0 P_{\text{LL}}(t), \quad (2)$$

where $\zeta_R(t)$ is the time dependent rotational friction and f_L^0 is a measure of the orientational "caging" and is given by

$$f_L^0 = 1 - \frac{\rho}{4\pi} c_{110}(k=0), \quad (3)$$

where $c_{110}(k)$ is the Fourier transform of the (110) component of the direct correlation function,[10] k_B is Boltzmann's constant, ρ is number density, and T is the temperature. This equation can be solved by Laplace transformation to obtain the following expression:

$$\frac{\hat{P}_{\text{LL}}(z)}{P_{\text{LL}}(t=0)} = \frac{z + \hat{\zeta}_R(z)}{z[z + \hat{\zeta}_R(z)] + 2f_L^0/\tau_I^2}, \quad (4)$$

where a caret on the top of a variable denotes Laplace transformation with z as the Laplace frequency conjugate to time and $\tau_I = (I/k_B T)^{1/2}$.

In order to proceed further we need to find $c_{110}(k)$ and the frequency dependent rotational friction. The first one can be obtained by mapping the Stockmayer fluid into a system of dipolar hard spheres for which it is safe to use Wertheim's MSA (mean spherical approximation) solution[11] for the polarity considered in the simulations of Neria and Nitzan[6] (the same may not be appropriate for the simulations of Perrera and Berkowitz[5] who simulated a liquid of much higher polarity). The mapping is performed as follows. A dipolar hard sphere in the fluid is characterized by only two dimensionless quantities, reduced dipole moment μ_{HS}^*, which is defined

$$\mu_{\text{HS}}^{*2} = \frac{\mu^2}{k_B T \sigma_{\text{HS}}^3}, \quad (5)$$

and reduced density $\rho_{\text{HS}}^* = \rho \sigma_{\text{HS}}^3$, where μ is the magnitude of the dipole moment of a Lennard-Jones atom. σ_{HS} is the diameter and ρ_{HS} is the number density of the hard sphere fluid. We use the Verlet–Weis scheme[12] of implementing the Weeks–Chandler–Andersen (WCA) perturbation theory[13] to find the density and temperature dependent effective hard sphere diameter σ_{HS} which maps the Lennard-Jones system into the hard sphere fluid. This procedure is expected to be reasonable at high densities. We find that for Neria–Nitzan system,[6] the corresponding hard sphere diameter is 1.01 σ_{LJ}. The Stockmayer fluid simulated by Neria and Nitzan is characterized by the following reduced parameters:

$$\rho^* \equiv \rho \sigma_{\text{LJ}}^3 = 0.81, \quad T^* \equiv k_B T/\epsilon = 1.23,$$
$$\mu^* = (\mu^2/\epsilon \sigma_{\text{LJ}}^3)^{1/2} = 1.32. \quad (6)$$

It is now straightforward to calculate the values of the reduced dipole moment and density of the corresponding hard sphere fluid. We find that $\mu_{\text{HS}}^* = 1.17$ and $\rho_{\text{HS}}^* = 0.83$. The direct correlation function and relaxation times have been calculated with these values.

We next proceed to find the frequency dependent rotational friction. As noted earlier, the only source of friction in the Stockmayer fluid is the dielectric friction. Fortunately, we have a fairly reliable way to calculate this

TABLE I. The comparison between theoretical and simulated values of τ_G which is obtained by fitting the calculated numbers for initial decay of solvation energy time correlation function $S(t)$ to a Gaussian form, exp $[-(t/\tau_G)^2]$. The simulated values are taken from Table I of Neria and Nitzan (Ref. 6). The time constant has been scaled by the inertial time τ_I.

I^*	p	τ_I (ps)	τ_G/τ_I (Simulation)	τ_G/τ_I (Theory)
0.038	0.019	0.41	0.42	0.44
0.25	0.125	1.05	0.33	0.35
0.50	0.25	1.49	0.28	0.29
For translationally immobile solvent				
			0.50	0.47

friction. This method makes use of the following exact relation between the friction and the angular velocity correlation function

$$\hat{\psi}_R(z) = \frac{\psi_R(t=0)}{z + \hat{\zeta}_R(z)}, \quad (7)$$

where $\hat{\psi}_R(z)$ is the Laplace transform of the angular velocity correlation function, $\psi_R(t)$. At short times the velocity correlation function can be well approximated by the following Gaussian form

$$\psi_R(t) = \psi_R(t=0)\exp(-\tfrac{1}{2}\Omega_R^2 t^2), \quad (8)$$

where Ω_R is the orientational Einstein frequency. The OEF can be expressed exactly in terms of the orientational pair correlation functions of the dipolar liquid[8]

$$\Omega_R^2 = \frac{\rho k_B T \mu^{*2}}{3I\pi} \int_0^\infty dq\, q j_1(q)[h_{110}(q) + h_{111}(q)], \quad (9)$$

where $j_1(q)$ is the spherical Bessel function of order unity and $h_{llm}(q)$ are the Fourier transforms of the orientational pair correlation functions.[10] We shall approximate the Einstein frequency of the Stockmayer fluid by that of an MSA dipolar hard sphere fluid with the transformations discussed above. We emphasize that this is a reasonable approximation at high density. Furthermore, the mistakes made in these approximations are expected to be within the uncertainties of the computer simulations. We find that for the parameters used by Neria and Nitzan, the value of OEF is equal to $1.47/\tau_I$, where the inertial time τ_I [$= (I/k_B T)^{0.5}$] is equal to 0.41 ps. Thus the initial decay of the angular velocity correlation function is predicted to be exp $[-1.08t^2/\tau_I^2]$. This could be easily tested in simulations. Unfortunately, no results on unperturbed solvent dynamics was presented in Ref. 6.

We have calculated the Gaussian decay rate τ_G by fitting the initial part of the calculated decay of the long wavelength polarization to a Gaussian form. We find that $\tau_G = 0.46\tau_I$ which is to be compared with the value $0.5\ \tau_I$ reported by Neria and Nitzan.[6] When the contributions of other modes are included, the calculated relaxation becomes slower and the agreement further improves, as discussed below (also, see Table I). Note that in the simulations of Neria and Nitzan (and also in Perera and Berkowitz) τ_I is very small, equal to 0.41 ps. So, the pre-

dicted τ_G is approximately 0.18 ps which is clearly a very short time. The reason that such a short time is important lies in the nature of the system studied—orientational motion of a spherical molecule with only dielectric friction as the retarding force can indeed be very fast. The relaxation is further accelerated here because the relevant motion is collective which relaxes under the influence of a collective polarization potential which is rather large for the $k=0$ mode. So, the relaxation is driven to proceed at an astronomically fast rate. Note that both H_2O and CH_3CN are small, nearly spherical molecules which are also in the underdamped limit of momenta relaxations. So, one expects the inertial decay to play a dominant role as indeed have been observed in simulations[1] and experiments.[2]

We would like to point out here that the above interpretation of the dominance of the initial solvation by the collective, $k=0$, polarization mode is in excellent agreement with the calculations and observations of Maroncelli.[1] Maroncelli[1] computed the relaxation of the collective longitudinal moment which is defined in his article by

$$\phi_L(\mathbf{k},t) \equiv \frac{\langle \mathbf{M}_L(-\mathbf{k},0)\cdot\mathbf{M}_L(\mathbf{k},t)\rangle}{\langle |\mathbf{M}_L(\mathbf{k})|^2\rangle}, \quad (10)$$

with

$$\mathbf{M}_L(\mathbf{k},t) \equiv \sum \mathbf{k}\mathbf{k}\mu_\alpha(t)\exp[i\mathbf{k}\cdot\mathbf{r}_\alpha(t)], \quad (10a)$$

where $\mu_\alpha(t)$ is the dipole moment of molecule α at time t. It was observed that for the longest mode that could be studied, $\Phi_L(k=k_{\min}, t)$ and $S(t)$ were nearly identical. In addition, the oscillations of the two functions were similar. The largest difference between the two was seen in the long time behavior where $\Phi_L(k=k_{\min}, t)$ decayed to zero much more rapidly than $S(t)$. Maroncelli[1] further suggested that the difference in the long time behavior between the two is because in the long time $S(t)$ is dominated by slow intermediate k ($k_{\mathrm{int}} \simeq 2\pi/\sigma$, σ is solvent molecular diameter) dynamics which is diffusive. The theoretical calculations of this article are in total agreement with the results and the observations of Maroncelli.[1]

Another important point to note is that solvation is not given by single particle inertial decay. This was also observed by Maroncelli [see Fig. 20(a) of Ref. 1]. The reason for this is rather simple—the relevant motion is the one which leads to polarization relaxation. Therefore, we must consider underdamped motion in a polarization potential. We shall show below that our theory correctly (and quantitatively) explains this rather complex dependence of τ_G on τ_I.

In order to check the robustness of the above description, we have also used a different prescription for calculating the frequency dependent friction. We assumed that in the short time, $\zeta_R(t)$ can be given by the following Gaussian form:

$$\zeta_R(t) = \Omega_R \exp[-(t/\tau_K)^2] \quad (11)$$

with the simplest approximation that $\tau_K = \tau_I$. The results for the initial decay [up to the value 0.5 of $S(t)$] differ insignificantly from the above, more accurate, analysis.

The initial decay is insensitive to the form of friction because it is very small at short times. Even if we set the value of friction to zero, the decay is not significantly perturbed (although the agreement between theory and simulation gets somewhat worse). However, the decay is quite sensitive to the value of the caging parameter f_L^0. This and the good agreement observed in the present study with the simulations seem to further substantiate the suggestion that the observed short time response is the response of the collective excitonic mode of the dipolar liquid. Since the value of the friction is very small it is more appropriate to call it a dipolaron.

As an extra check on the consistency of our calculational scheme, we have carried out a limited molecular dynamics simulation of Neria–Nitzan system and obtained the value of the orientational Einstein frequency directly. We find that the simulated result agreed with our calculated value within 1%. It lends additional support to our theory.

We next describe the complete theoretical calculation (with translation included) which is a bit more complicated. The wave vector dependent longitudinal polarization is given as a function of frequency (z) by the following equation:[3]

$$\hat{P}_L(k,z) = P_L(k,t=0) \left[z + \frac{2f_L(k)}{z+\hat{\zeta}_R(z)} + \frac{pq^2 f_L(k)}{z+\hat{\zeta}_T(z)} \right]^{-1}, \quad (12)$$

where $p = I/m\,\sigma^2$, $q = k\sigma$ and frequency is in the unit of τ_I. $\hat{\zeta}_T(z)$ is the frequency dependent translational friction. We need the high frequency part of this friction. As before we find this quantity by using the memory function equation [analog of Eq. (6) for the translational case]. The initial decay of the velocity correlation function is now approximated by

$$\psi(t) = \psi(t=0)\exp(-\tfrac{1}{2}\Omega_0^2 t^2), \quad (13)$$

where Ω_0 is the usual Einstein frequency for translational motion,[9] defined as the mean-square force on a tagged molecule. For a monatomic system this is given by the following expression:[9]

$$\Omega_0^2 = \frac{\rho}{3m} \int d\mathbf{r}\, g(r)\nabla^2 u(r), \quad (14)$$

where $u(r)$ and $g(r)$ are the interaction potential and the radial distribution function of the system, respectively. The most of the contribution to Einstein frequency comes from the short range part of the potential, so we have approximated the potential $u(r)$ in Eq. (12) by a Lennard-Jones potential. With this approximation it is straightforward to evaluate this quantity and we find that for the present system, Ω_0 is equal to 6.7×10^{12} s^{-1}. A separate molecular dynamics simulation provides a value 6.2×10^{12} s^{-1}. We have used the former value in order to be consistent, although the difference is entirely negligible.

The time dependent solvation energy is given by the following expression:[14]
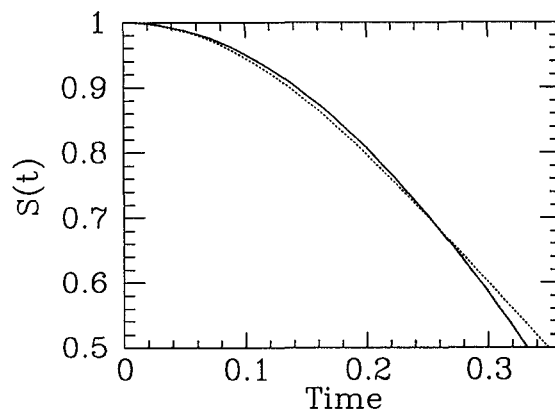

FIG. 1. The calculated solvation energy time correlation function (solid line) is compared with the simulated correlation function (dashed line) obtained by Neria and Nitzan (Ref. 6, Fig. 4). The theoretical results are obtained by using Eq. (15) of the text. The value of the translational parameter p is 0.019. The rest of the parameter values and the calculational procedure have been discussed in the text.

$$E_{\text{solv}}(t) \propto \int d\mathbf{k} \left[1 - \frac{1}{\epsilon(k)} \right] \frac{\sin^2 k}{k^2} \left[\frac{P(k,t)}{P(k,t=0)} \right]. \quad (15)$$

The wave vector dependent dielectric function $\epsilon(k)$ is obtained from that of the dipolar hard spheres at the corresponding density, as discussed previously.[14]

III. RESULTS

In Table I we have compared the calculated values of the Gaussian time τ_G [obtained by fitting the calculated $S(t)$ to a Gaussian form] with the values given by Neria and Nitzan.[6] We have fitted the initial decay only by keeping up to 0.5 of $S(t)$. Note that the agreement between theory and simulation is very good. In fact, we should not have expected such good agreement in view of the approximations made here and also the uncertainties inherent in simulations. The reason for such a good agreement is that the solvation dynamics is very sensitive only to the caging parameter f_L. The decay is, of course, sensitive to the inertial time τ_I; but this dependence has been absorbed through the scaling of the time.

We would like to point out here that the theory correctly predicts the weakening of the dependence of the decay on τ_I as the value of the translational parameter p is increased. This indicates the increased role of the translational modes at large p, as expected.

In Fig. 1 we show the comparison of the calculated result with the computer simulation of Neria and Nitzan.[6] At short times, the agreement between theory and simulation is excellent. The deviations start at long times which can be easily understood. At long times, the diffusive modes begin to play a role in the solvation so the decay slows down. It would be interesting to perform a full calculation with a frequency dependent friction which is reliable at all frequencies. Clearly, the solvent polarization potential makes a significant contribution in the initial decay which is much faster than the free inertial decay.

At this point we note that the contention of Cho et al.[4] that solvation dynamics measures the linear response is supported in the present study by the observed excellent agreement between the calculated and the simulated results. The reason is that *in the short time the decay is controlled primarily by the k=0 mode which being a macroscopic mode is least likely to be perturbed by the solute.* While this is comforting, a similar demonstration of linear solvent response for the nearest-neighbor dynamics is not available. This can be accomplished by studying the observed long time slow decay which is expected to be controlled by the diffusive relaxation.

IV. CONCLUSION

We conclude this article with the following comments:

(1) The present calculations seem to confirm that the ultrafast solvation observed in recent computer simulations can be described in terms of a collective excitation. It is amusing to note in this connection that the first molecular dynamics simulation of Stockmayer liquid was carried out by Pollock and Alder[15] to study collective excitation itself.

(2) It was demonstrated earlier[3] that the present theory can also describe the biphasic solvation observed in computer simulations and in experiments. However, a quantitative explanation of the full time dependence of $S(t)$ requires an accurate description of the frequency dependence of the friction over the whole frequency range. We suggest that this be calculated by a computer simulation for the Stockmayer fluid. This will allow a full comparison with the theory.

(3) The orientational Einstein frequency (OEF) is a property of the pure liquid. We have shown elsewhere that in the absence of any nondipolar angle dependent interaction, orientational Einstein frequency is exactly equal to the dipolar solvation energy of a dipole in a neat liquid.[8] Therefore, OEF can be calculated by an equilibrium simulation for a Stockmayer liquid.

(4) It is important to note that the usual, macroscopic friction does not at all enter in the theoretical description of the short time dynamics. Thus, the theory needs no information about the diffusion coefficients which will, however, be needed in the description of the long time dynamics. As suggested by Xu and Stratt,[9] we can find a rough estimate of the rotational or translational diffusion coefficients by integrating the short time, Gaussian, representations of the respective velocity correlation functions. In the model of Neria and Nitzan, this gives a value of rotational diffusion coefficient equal to 2.4×10^{12} s^{-1} and a value of translational diffusion coefficient equal to 5.25×10^{-5} cm^2 s^{-1}. We suspect that the value of the rotational diffusion coefficient obtained by this method is a factor of 2–3 times too high, indicating that the negative part of the angular velocity correlation function is important in this system.

(5) The large contribution of the inertial component is a direct consequence of the Stockmayer potential which offers only a small rotational friction. In most organic liquids this inertial contribution is expected to be less important because the presence of short range angle dependent

potential will tend to make orientational Einstein frequency much larger which can damp out the inertial motion. However, it seems that this inertial component is also large for water and acetonitrile.

(6) The present calculations are purely classical, as also are the computer simulations. At short times, the quantum effects can be significant.

(7) Finally, we address the issue raised by the different interpretation of Cho et al.[4] for the initial Gaussian decay of $S(t)$. The situation seems to be rather paradoxical because the model of Cho et al. is rather different, at least in spirit, from the present model and interpretation. The reason for the apparent agreement of Cho et al.'s model with the simulation of Maroncelli, therefore, needs to be understood. As we have already pointed out the present calculation also agrees with the simulation of Maroncelli, especially in that it quantitatively explains the observed difference between the *free* inertial decay and the solvation correlation function. In this situation, we have the following suggestions. A detailed computer simulation must be carried out to check the predictions of the two models. Since our model offers various specific predictions, its verification should be straightforward. Second, the model of Cho et al. contains some parameters which are found by fitting to experiments. It is necessary to have estimates of these parameters from the model itself so that they can also be tested against computer simulations. Finally, we note that the expressions of $S(t)$ that these two models give rise to are not very different from each other; the main difference is that of interpretation. In fact, Eq. (2) of the present article can be converted to a Langevin equation for the orientational motion of the individual dipoles. Therefore, the main difference from the picture of Cho et al. is the presence of a collective potential in the present model. No "unphasing" of motion is necessary for ultrafast solvation.

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