Monte Carlo simulation of orientational effects on direct energy transfer

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The donor ensemble excitation decay is obtained by a Monte Carlo simulation for the three-dimensional case. Donor and acceptor reorientational motions are explicitly considered within the isotropic diffusion model. Allowance is made for donor and acceptor different rotational rates. The orientation dependent part of the decay is fully contained in the factor $\langle (\overline{\kappa^2})^{1/2}\rangle$ which is the ensemble average of the square root of the finite time average of the usual orientational factor κ^2. The time dependence of $\langle (\overline{\kappa^2})^{1/2}\rangle$ is evaluated by a Monte Carlo simulation procedure for several relative mobilities of the donor–acceptor pair and finally captured in a simple, one-parameter formula.

I. INTRODUCTION

Förster-type energy transfer[1] is a well established mechanism of excitation transfer between singlet states.[2] The rate constant for this dipole–dipole interaction contains an orientational factor κ^2 which is often taken as the ensemble average value of the isotropic distribution, 2/3. This corresponds to the dynamic limit, where rotation of both donor and acceptor is fast compared to transfer.[3] Since κ^2 will in general be a random function of time, owing to random changes in donor and acceptor orientations, it is not clear why a time-independent value should replace $\kappa^2(t)$ and more so in the dynamic limit, where fluctuations occur very frequently. The answer is that, while the (highly) time-dependent rate constant effectively contains $k^2(t)$, and not 2/3, the excitation decay contains the finite time average of the rate constant (see Sec. II) and therefore the finite time average of the orientational factor $\overline{\kappa^2}$; if rotation is fast compared to transfer, and provided both molecules of the pair rotate, all values of κ^2 are sampled in a short time, and the finite time average equals the ensemble average from the very beginning of the decay. Therefore, when 2/3 is substituted for $\kappa^2(t)$ in the rate constant, one no longer has a rate constant, but rather the time coefficient of the excitation decay. This has been a somewhat neglected point. In the general case, the orientational factor appearing in the decay is a time-dependent quantity, since the usual κ^2 should be replaced by $\overline{\kappa^2}$. This was previously done by Knoester and Van Himbergen[4] with the Huber, Hamilton, and Barnett excitation decay law,[5] that takes into account back transfer in an approximate way.

In this work, direct energy transfer is examined in some detail from a stochastic viewpoint. In contrast to Ref. 4, donor and acceptor are allowed to rotate at different rates, and a closer connection is made with experimental parameters. In Sec. II the general theoretical framework is presented, with emphasis on the stochastic basis of the excitation decay. In the limit of low concentrations, the usual Förster decay is retrieved, but now with the time-dependent orientational factor in. In Sec. III the simulation procedure, based on the discrete jump model, is outlined. The results of the simulation are presented and discussed in Sec. IV. The main results are finally summarized in Sec. V. The unit interval, uniform pseudorandom number generator used is described in Appendix B.

II. THEORY

A. Survival probability and excitation decay

The probability that a certain donor molecule, excited at $t = 0$, is still excited at a later time t (survival probability) is given by

$$P(t) = \exp\left[-\int_0^t w(t')dt' \right], \tag{2.1}$$

where $w(t)$ is the time-dependent rate constant. This follows directly from the deterministic rate law

$$\frac{dN}{dt} = -w(t)N, \tag{2.2}$$

N being the number of excited donors, by putting $P = N/N_0$, where N_0 is the initial number of excited donors.

Equation (2.2) is however only approximate, since N is a discrete random variable.[6] A satisfactory derivation of Eq. (2.1) must therefore rest on stochastic grounds. Ishida[7] gave such a derivation under the Master equation formalism. A simpler, and perhaps physically more appealing derivation is the following: let $P(\Delta t\,|t_0)$ be the probability that the donor is still excited at $t = t_0 + \Delta t$, given that it was excited at t_0. If Δt is small, then a truncated power expansion in Δt yields

$$P(\Delta t\,|t_0) = 1 + P'(0|t_0)\Delta t. \tag{2.3}$$

Defining the rate constant as[8] $w(t_0) = -P'(0|t_0)$ one gets

$$P(\Delta t\,|t_0) = 1 - w(t_0)\Delta t. \tag{2.4}$$

After a finite time lapse $t = n\Delta t$, the probability that the donor is still excited is clearly

$$P(t) = \prod_{i=1}^{n} [1 - w(i\Delta t)\Delta t]. \tag{2.5}$$

The exact relation being obtained for $n \to \infty$:

$$P(t) = \lim_{n\to\infty} \prod_{i=1}^{n} \left[1 - w\left(\frac{it}{n}\right)\frac{t}{n}\right], \tag{2.6}$$

or

$$P(t) = \exp\left\{\lim_{n\to\infty} \sum_{i=1}^{n} \ln\left[1 - w\left(\frac{it}{n}\right)\frac{t}{n}\right]\right\}, \tag{2.7}$$

which reduces to

$$P(t) = \exp\left[-\lim_{n\to\infty} \sum_{i=1}^{n} w\left(\frac{it}{n}\right)\frac{t}{n}\right] \tag{2.8}$$

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equivalent to Eq. (2.1) by the definition of Riemann integral.

If N_0 molecules, initially excited, decay independently, then the probability that, at time t, N are still excited must be given by the binomial law

$$P(N,t) = \binom{N_0}{N}[P(t)]^N[1-P(t)]^{N_0-N}. \tag{2.9}$$

For large N_0, N Stirling formula yields,

$$P(N,t) = \left(\left[\frac{P(t)}{N/N_0}\right]^{N/N_0}\left[\frac{1-P(t)}{1-N/N_0}\right]^{1-N/N_0}\right)^{N_0} \tag{2.10}$$

and, for constant t, Eq. (2.10) peaks very sharply at

$$N = N_0P(t), \tag{2.11}$$

which is also the mean value of $P(N,t)$. Thus, for a large number of molecules, the excitation decay becomes deterministic, and the fraction $N(t)/N_0$ equals the survival probability $P(t)$ as required by the frequency interpretation of probability, and $N(t)$ equals the mean value of $P(N,t)$, as expected from the law of large numbers.

B. Excitation decay

Direct energy transfer from an excited donor to acceptors embedded in condensed media has been studied extensively for several geometries and dimensions.[1,9] A unified approach was presented by Blumen and Manz.[10] We will concentrate here on the three-dimensional case. Within the dipole–dipole approximation, and for low acceptor concentration, the well-known Förster decay is retrieved. For the sake of completeness, this decay will be briefly rederived with special emphasis on the time dependence of the orientational factor. It is assumed that no translational diffusion takes place.

The rate constant for energy transfer is, in the dipolar approximation,

$$w(r,t) = \kappa^2(t)w(r), \tag{2.12}$$

where κ^2 is the orientational factor, given by Eqs. (2.14) or (2.15) and $w(r)$ is

$$w(r) = \frac{3}{2}\frac{1}{\tau}\left(\frac{R_0}{r}\right)^6, \tag{2.13}$$

where r is the donor–acceptor distance, τ is the donor lifetime, and R_0 is the Förster critical radius.[1] Equation (2.12) is valid only if donor and acceptor spectra are characterized by a single transition dipole in the region of spectral overlap.[11] Whenever mixed polarization occurs, either in acceptor's absorption or in donor's emission, the orientational dependence of the rate constant is greatly diminished.[12] In the following, Eq. (2.12) is assumed to hold. The orientational factor κ^2 is given by[1–4]

$$\kappa^2 = [3(\mathbf{n}\cdot\mathbf{d}_1)(\mathbf{n}\cdot\mathbf{d}_2) - \mathbf{d}_1\cdot\mathbf{d}_2]^2, \tag{2.14}$$

where $\mathbf{d}_1$ and $\mathbf{d}_2$ are unit vectors along donor and acceptor transition dipole directions, and $\mathbf{n}$ is the unit vector along the direction joining donor and acceptor. An equivalent formula, but depending on two angles only, is[13]

$$\kappa^2 = (3\cos^2\theta + 1)\cos^2\omega, \tag{2.15}$$

where θ is the angle between $\mathbf{d}_1$ and $\mathbf{n}$ and ω is the angle between the acceptor transition dipole and the electric field produced by the donor dipole at the acceptor.[14] The orientational factor, and thus the rate constant, is time dependent owing to random rotations performed by the donor and by the acceptor. κ^2 is therefore a random function of time, i.e., a stochastic process.

Substitution of Eq. (2.12) in Eq. (2.1) yields

$$P(r,\overline{\kappa^2},t) = \exp[-\overline{\kappa^2}w(r)t], \tag{2.16}$$

where $\overline{\kappa^2}$ is the finite time average of κ^2,

$$\overline{\kappa^2}(t) = \frac{1}{t}\int_0^t \kappa^2(t')dt'. \tag{2.17}$$

In order to obtain the macroscopic excitation decay $\rho(t)$ one merely notes that the fundamental equation derived by Blumen and Manz,[10]

$$\rho(t) = \prod_{i=1}^{N}[1-\alpha+\alpha P_i(t)], \tag{2.18}$$

where α is the fraction of the N lattice sites that is occupied by acceptors and $P_i(t)$ is given by Eq. (2.16) with $r = r_i$, has to be averaged over the $\overline{\kappa^2}$,

$$\rho(t) = \int_0^4\int_0^4\cdots\int_0^4 f(\overline{\kappa_1^2},\overline{\kappa_2^2},\ldots,\overline{\kappa_N^2}) \times\prod_{i=1}^{N}[1-\alpha+\alpha P_i(\overline{\kappa_i^2},t)]\,d\overline{\kappa_i^2}. \tag{2.19}$$

Assuming that the sites are uncorrelated and equivalent with respect to orientational mobility,

$$f(\overline{\kappa_1^2},\overline{\kappa_2^2},\ldots,\overline{\kappa_N^2}) = f(\overline{\kappa_1^2})f(\overline{\kappa_2^2})\cdots f(\overline{\kappa_N^2}), \tag{2.20}$$

hence Eq. (2.19) becomes

$$\rho(t) = \prod_{i=1}^{N}[1-\alpha+\alpha\bar{P}_i(t)], \tag{2.21}$$

where

$$\bar{P}_i(t) = \int_0^4 f(\overline{\kappa^2})P_i(\overline{\kappa^2},t)\,d\overline{\kappa^2}. \tag{2.22}$$

In this way, the usual decay law valid for low α,

$$\rho(t) = \exp\left\{-N\int_0^\infty g(r)[1-P(r,t)]dr\right\}, \tag{2.23}$$

where $g(r)$ is the distance distribution function, becomes

$$\rho(t) = \exp\left\{-N\int_0^\infty g(r)[1-\bar{P}(r,t)]dr\right\} \tag{2.24}$$

or, for the dipolar interaction in three-dimensional space, where

$$Ng(r) = 4\pi nr^2, \tag{2.25}$$

n being the number density, one obtains

$$\rho(t) = \exp\left\{-\left(\frac{3\pi}{2}\right)^{1/2}\frac{c}{c_0}\langle(\overline{\kappa^2})^{1/2}\rangle\left(\frac{t}{\tau}\right)^{1/2}\right\}, \tag{2.26}$$

where

$$\langle(\overline{\kappa^2})^{1/2}\rangle = \int_0^4 f(\overline{\kappa^2})(\overline{\kappa^2})^{1/2}d\overline{\kappa^2} \tag{2.27}$$

and

$$c_0 = 3/4\pi R_0^3 N_A, \tag{2.28}$$

where N_A is the Avogadro constant.

Equation (2.26) is the familiar Förster decay law, apart from the factor $\langle (\overline{\kappa^2})^{1/2}\rangle$. Note that this factor is time dependent, since $f(\overline{\kappa^2})$ is in fact $f(\overline{\kappa^2},t)$. The orientational dependence is then contained in the factor $\langle (\overline{\kappa^2})^{1/2}\rangle$.

In the dynamic limit, where rotation of donor and acceptor is fast compared to the decay time scale, the time average becomes equal to the ensemble average (ergodicity) since the very beginning and, for all times of interest, one can put $\overline{\kappa^2} = \langle \kappa^2 \rangle$, hence

$$\langle (\overline{\kappa^2})^{1/2}\rangle = (2/3)^{1/2} = 0.81649 \cdots \tag{2.29}$$

on the other hand, in the static limit[15] one has $\overline{\kappa^2} = \kappa^2$, hence

$$\langle (\overline{\kappa^2})^{1/2}\rangle = \langle |\kappa| \rangle = [\ln(2+\sqrt{3})/2\sqrt{3} + 1]/2 = 0.690\,08 \cdots . \tag{2.30}$$

In the general case, the factor $\langle (\overline{\kappa^2})^{1/2}\rangle$ is time dependent: at $t = 0$, the static limit is verified; for time larger than zero, an intermediate regime is obeyed, with $\langle (\overline{\kappa^2})^{1/2}\rangle$ asymptotically approaching a constant value. This was already pointed out by Knoester and Van Himbergen.[4] They have however assumed that donor and acceptor had the same rotational behavior. This need not be so even with identical molecules, since donor and acceptor, being in different electronic states, may have different shapes and/or interactions with solvent.

The simplest, but still meaningful model for molecular rotation is the isotropic diffusion model.[16] Even at this level, an analytical calculation of $f(\overline{\kappa^2},t)$ seems impossible. Nevertheless, this function can be obtained for some special situations. For $t = 0$ (static limit) one has $f(\kappa^2)$, given by[17]

$$f(\kappa^2) = \frac{1}{2\sqrt{3\kappa^2}}[\ln(2+\sqrt{3}) - H(\kappa^2 - 1)\ln(\sqrt{\kappa^2} + \sqrt{\kappa^2 - 1})]. \tag{2.31}$$

Where H is the Heaviside function. If both molecules of the pair are mobile, then (dynamic limit)

$$\lim_{t\to\infty} f(\overline{\kappa^2},t) = \delta(\overline{\kappa^2} - 2/3), \tag{2.32}$$

i.e., regardless of initial relative orientation, $\overline{\kappa^2}$ will always end up as 2/3 (see Fig. 4).

This is, as mentioned, a consequence of the ergodicity of the stochastic process. If, however, only one of the two molecules rotates,

$$\lim_{t\to\infty} f(\overline{\kappa^2},t) = \begin{cases} (\overline{\kappa^2} - 1/3)^{-1/2}/2, & \text{if } 1/3 < \overline{\kappa^2} \leqslant 4/3 \\ 0 & \text{otherwise} \end{cases}, \tag{2.33}$$

as derived in Appendix A.

In this case the process is nonergodic, since the time evolution of $\overline{\kappa^2}$ is conditioned by the initial relative orientation of donor and acceptor (see also Fig. 4). The dynamic value of $\langle (\overline{\kappa^2})^{1/2}\rangle$, computed from Eq. (2.33), is now

$$\langle (\overline{\kappa^2})^{1/2}\rangle = \tfrac{1}{3} + \tfrac{1}{6}\ln(2+\sqrt{3}) = 0.796\,84 \cdots . \tag{2.34}$$

The time evolution of $\langle (\overline{\kappa^2})^{1/2}\rangle$ is a function of the reorientation rate of both donor and acceptor. It is assumed that molecular reorientation proceeds according to the isotropic diffusion model. In Sec. III the Monte Carlo method used to simulate molecular rotation and therefore, to obtain the time-dependent quantity $\langle (\overline{\kappa^2})^{1/2}\rangle$, is described.

III. THE SIMULATION PROCEDURE

Isotropic rotational diffusion was simulated using the discrete jump model,[16] where the molecule keeps its orientation for a certain interval of time, after which it rotates instantaneously by a finite angle. This model is characterized by τ_a, average time between jumps, and by the angular distribution $g(\alpha)$.

For small α, the model becomes diffusive, with a coefficient of rotational diffusion D given by[16]

$$D = \frac{\langle \alpha^2 \rangle}{4\tau_a} \tag{3.1}$$

or, in terms of the rotational correlation time τ_r,

$$\tau_r = \frac{2}{3}\frac{\tau_a}{\langle \alpha^2 \rangle}. \tag{3.2}$$

The probability of having n jumps in a given interval Δt is Poisson distributed, with mean $\Delta t/\tau_a$. The step used was $\Delta t = 0.1\,\tau_a$, so the probability of having two or more jumps in Δt is less than 0.5%. In this way the reduced time $t^* = t/\tau_r$ is related to the number n of steps by

$$t^* = 0.15\, n\langle \alpha^2 \rangle. \tag{3.3}$$

Donor and acceptor have, in general, different correlation times for rotation. In order to maintain the probability of multijump below 0.5%, Δt (and therefore t^*) must be defined in terms of the smaller τ_r. Accordingly, the average number of jumps in Δt will be $0.1q$ for the slowest molecule, where q is the ratio of the smaller to the larger correlation time. The probability of no jump in Δt is $\exp(-\mu)$, where μ is either 0.1 (fast rotating partner) or $0.1q$ (slow rotating partner). The probability of jump, is of course, $1 - \exp(-\mu)$. A unit inverval, uniform pseudorandom number generator (see Appendix B) was used to generate numbers between 0 and 1, and therefore to decide if rotation occurred or not. If it did, the molecule rotated by an angle α from the original position to a new one in a random direction. This was accomplished by generating a random axis in space, and then performing a rotation by δ around that axis. If the axis is defined by the unit vector (C_1,C_2,C_3) then the transformation matrix from the old to the rotated position is[18]

$$A = \begin{bmatrix} \cos\delta + (1-\cos\delta)C_1^2 & (1-\cos\delta)C_1C_2 - C_3\,\mathrm{sen}\,\delta & (1-\cos\delta)C_1C_3 + C_2\,\mathrm{sen}\,\delta \\ (1-\cos\delta)C_2C_1 + C_3\,\mathrm{sen}\,\delta & \cos\delta + (1-\cos\delta)C_2^2 & (1-\cos+\delta)C_2C_3 - C_1\,\mathrm{sen}\,\delta \\ (1-\cos\delta)C_3C_1 - C_2\,\mathrm{sen}\,\delta & (1-\cos\delta)C_3C_2 + C_1\,\mathrm{sen}\,\delta & \cos\delta + (1-\cos\delta)C_3^2 \end{bmatrix}. \tag{3.4}$$

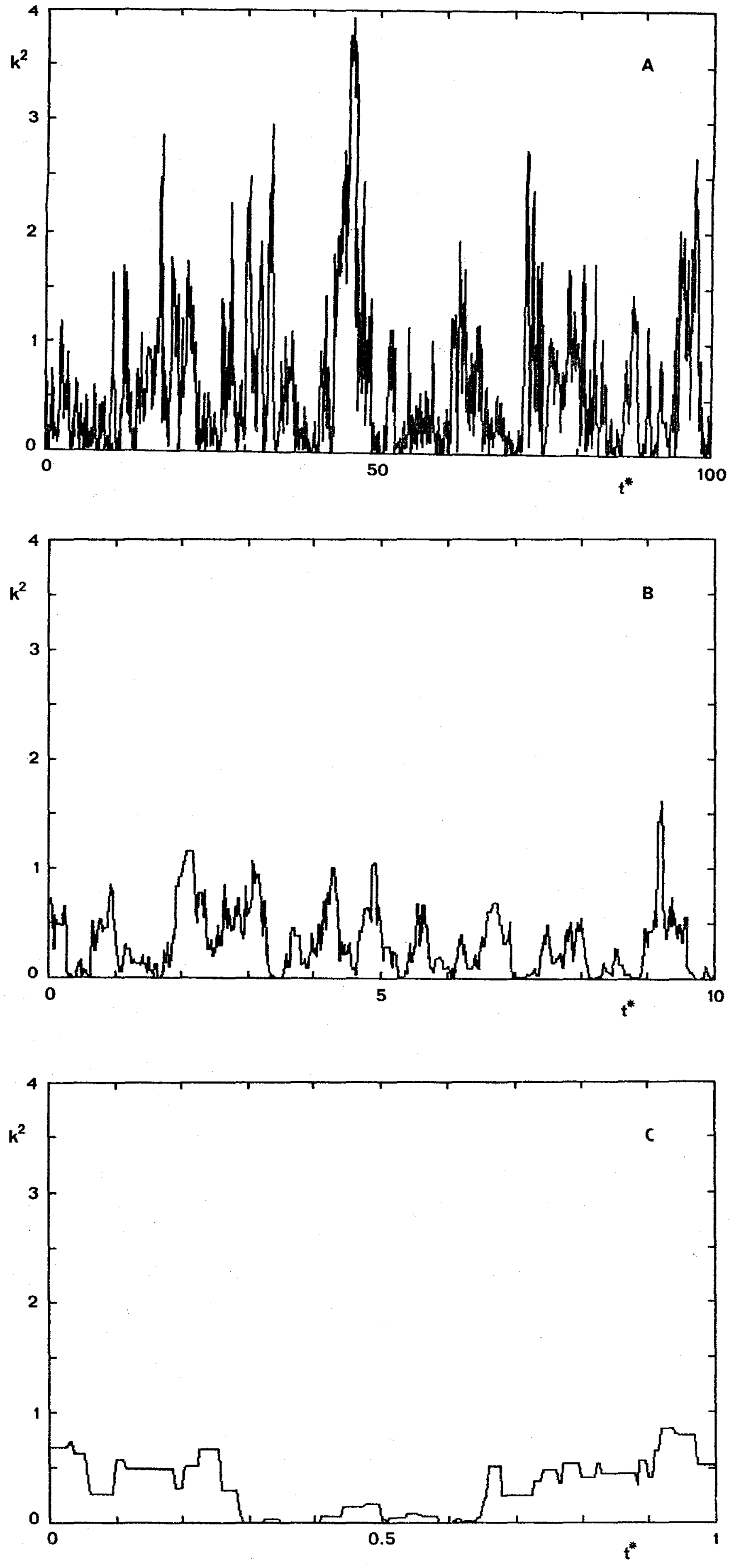

FIG. 1. A realization of the orientational factor when both partners have the same rotational mobility ($q = 1$). Time span is decreased from A to C.

For small δ one has (see Appendix C)

$$\langle \alpha^2 \rangle = \tfrac{2}{3}\,\delta^2. \tag{3.5}$$

Usually, δ was set to 10°. Check simulations with $\delta = 5°$ showed negligible variation.

Application of this procedure to both partners allowed the calculation of κ^2 [Eq. (2.14)] for each step. In each run, initial orientations were selected at random. The time-dependent double integral $\langle(\overline{\kappa^2})^{1/2}\rangle$ was evaluated as

$$\langle(\overline{\kappa^2})^{1/2}\rangle = \frac{1}{m}\sum_{i=1}^{m}\left[\frac{1}{n+1}\sum_{j=0}^{n}\kappa_i^2\left(\frac{jt}{m}\right)\right]^{1/2}, \tag{3.6}$$

with $m = 20\,000$ and $n = t/\Delta t$. The curves obtained are probably in error by less than 1%. Values for $t = 0$ provide a good test for accuracy, since the exact result $(\langle|\kappa|\rangle)$ is known. Deviations were smaller than 0.5% for all runs.

IV. RESULTS AND DISCUSSION

The orientational factor κ^2 is a stationary stochastic process. Its distribution function, independent of time, is given by Eq. (2.31). A particular realization of κ^2 is shown in Fig. 1 for $q = 1$, i.e., for donor and acceptor with equal mobility. It is seen that the near zero a value of κ^2 is, the more frequently it occurs. Values near four are exceedingly rare. If both molecules rotate, all realizations are essentially equivalent, since the memory of the initial orientation is rapidly lost. Therefore, the process is ergodic, and the time average of a single realization, $\overline{\kappa^2}$, will equal the ensemble average, $\langle\kappa^2\rangle$, for sufficiently long times, as expressed by Eq. (2.32). If, however, only one of the molecules of the pair is mobile $(q = 0)$ then the process is nonergodic, since the initial orientation is never completely forgotten. Two realizations of κ^2 with $q = 0$ are shown in Fig. 2, the top one corresponding

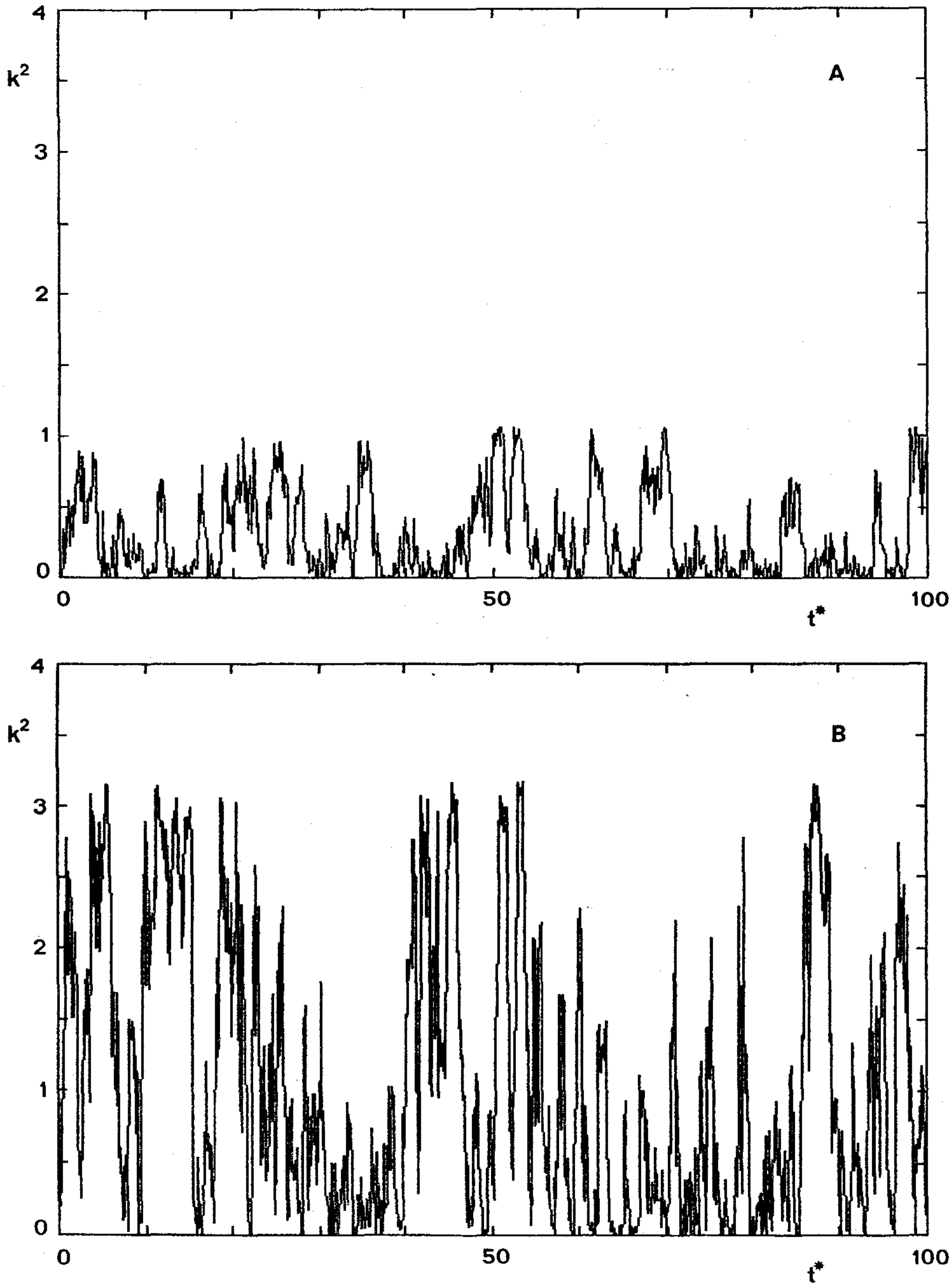

FIG. 2. Two realizations of the orientational factor when only one of the partners is mobile $(q = 0)$.

to an unfavorable initial orientation, and the bottom one corresponding to a favorable initial orientation. It is seen how these shape the time evolution of κ^2. It is well known that the memory of a stationary process $x(t)$ is quantitatively expressed by the autocorrelation function

$$c(t) = \frac{\langle x(t+t_0)x(t_0)\rangle - \langle x\rangle^2}{\langle x^2\rangle - \langle x\rangle^2}. \tag{4.1}$$

In the autocorrelations shown in Fig. 3, $\langle\kappa^2(t+t_0)\kappa^2(t_0)\rangle$ was averaged over 350 000 pairs. $\langle\kappa^4\rangle$ was computed by numerical integration of Eq. (2.31) and found to be 0.960 01. Since $\langle\kappa^2\rangle = 2/3$, the variance of κ^2 is 0.515 56. The autocorrelation function for $q = 1$ displays a correlation time of the order of τ_r, and for $t^* > 3$ is essentially zero. The autocorrelation function for $q = 0$ shows the same initial decay, but stabilizes at a residual, nonzero value. This indicates the existence of a definite correlation between κ^2 values taken at different times, even when well separated in

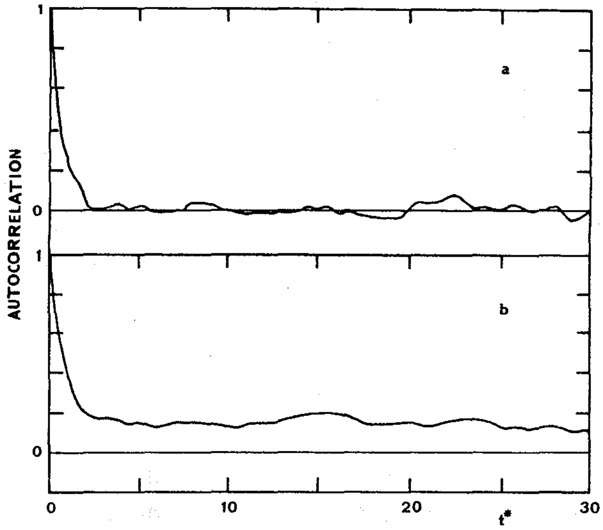

FIG. 3. Normalized autocorrelation function of the orientational factor $q = 1$ (A) and $q = 0$ (B).

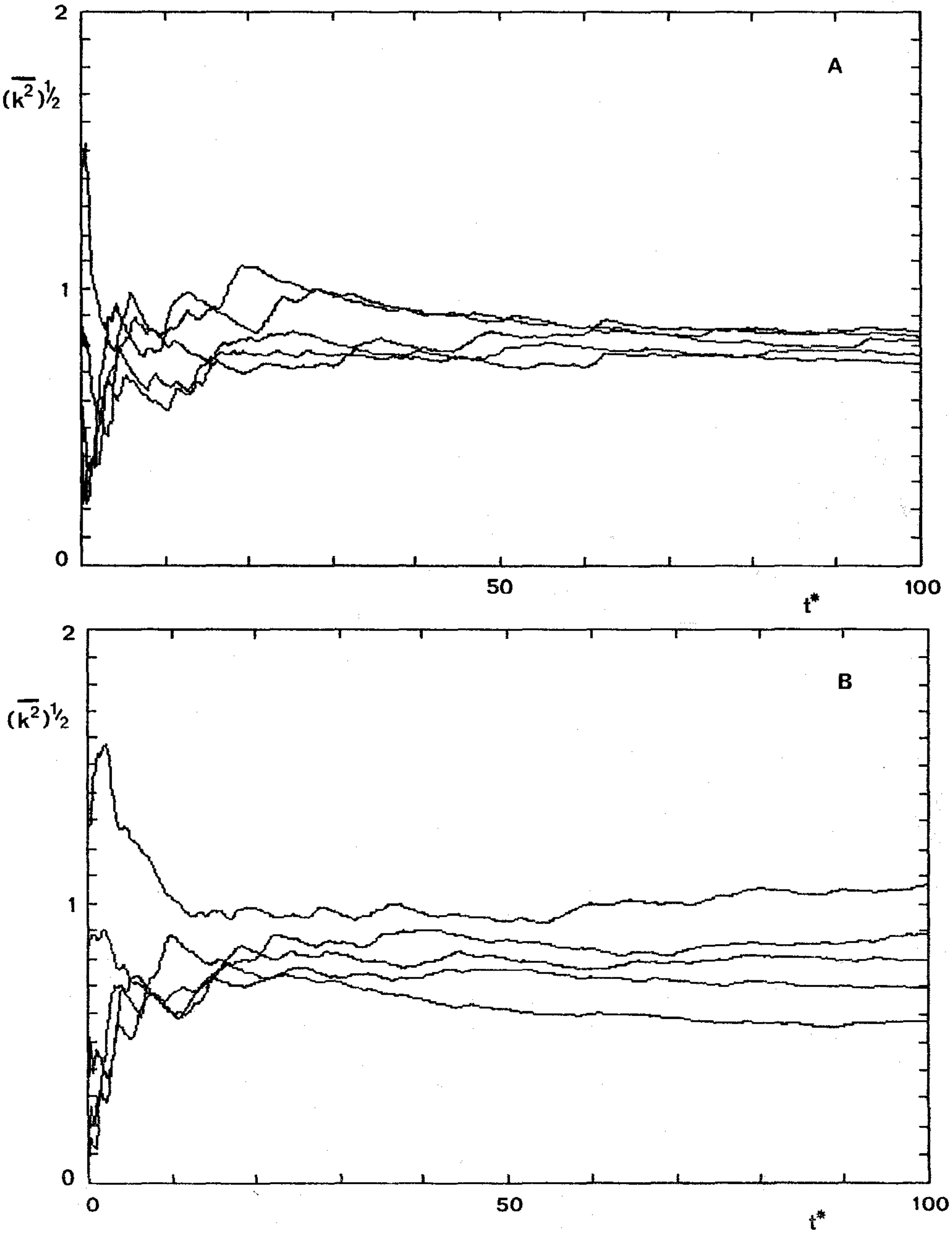

FIG. 4. Realizations of $(\overline{\kappa^2})^{1/2}$ for $q = 1$ (A) and $q = 0$ (B).

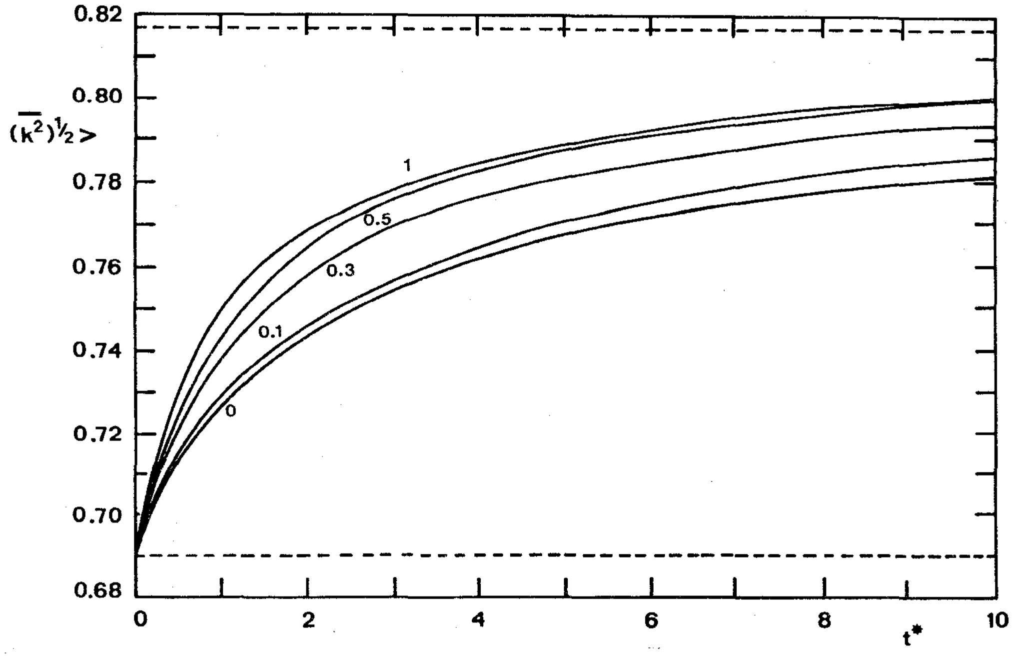

FIG. 5. Time dependence of $\langle(\overline{\kappa^2})^{1/2}\rangle$ for selected values of the relative mobility q.

time. Memory of the initial orientation is never completely lost.

The time average of κ^2, $\overline{\kappa^2}$, is also a stochastic process, but a nonstationary one. This is easily recognized in Fig. 4, where five realizations of $(\overline{\kappa^2})^{1/2}$ are depicted for $q = 0$ and for $q = 1$. For $q = 0$, $(\overline{\kappa^2})^{1/2}$ curves do not converge to a single value as $t^* \to \infty$. This is to be expected, given the limiting distribution of $\overline{\kappa^2}$, Eq. (2.33). For $q = 1$, on the contrary, all five realizations almost superimpose at $t^* = 100$, with values close to the expected limit, $(2/3)^{1/2}$.

The ensemble average of $(\overline{\kappa^2})^{1/2}$, $\langle(\overline{\kappa^2})^{1/2}\rangle$, is shown in Fig. 5 for some values of q. The curves with $q \neq 0$ approach the limiting value $(2/3)^{1/2}$, while the curve with $q = 0$ has as a limit the slightly lower value 0.7968... . From the figure it is apparent that the dynamic limit should, for all the curves displayed, be reached in less than about 50 τ_r.

Curves were well fitted by the empirical formula

$$y = \frac{a y_\infty t^* + y_0}{a t^* + 1}, \qquad (4.2)$$

where $y = \langle(\overline{\kappa^2})^{1/2}\rangle$ and a is the fitting parameter.

In Fig. 6 the simulated curve for $q = 1$ is compared to its fitting counterpart. For lower q values ($q \neq 0$) the fit was not so good, the average deviation never exceeding however 0.5%. For $q = 0$ and with $y_\infty = 0.7968...$ a fit comparable to that with $q = 1$ is again obtained. In Fig. 7 the parameter a is shown as a function of q. A least-squares fit to the pairs of $q > 0.1$ gives, with an average deviation of 6%,

$$a = -0.596\, q^2 + 1.076\, q + 0.285. \qquad (4.3)$$

Equations (4.2) and (4.3), though approximate and restricted to either $q = 0$ or $q > 0.1$ are probably as precise as needed for most purposes.

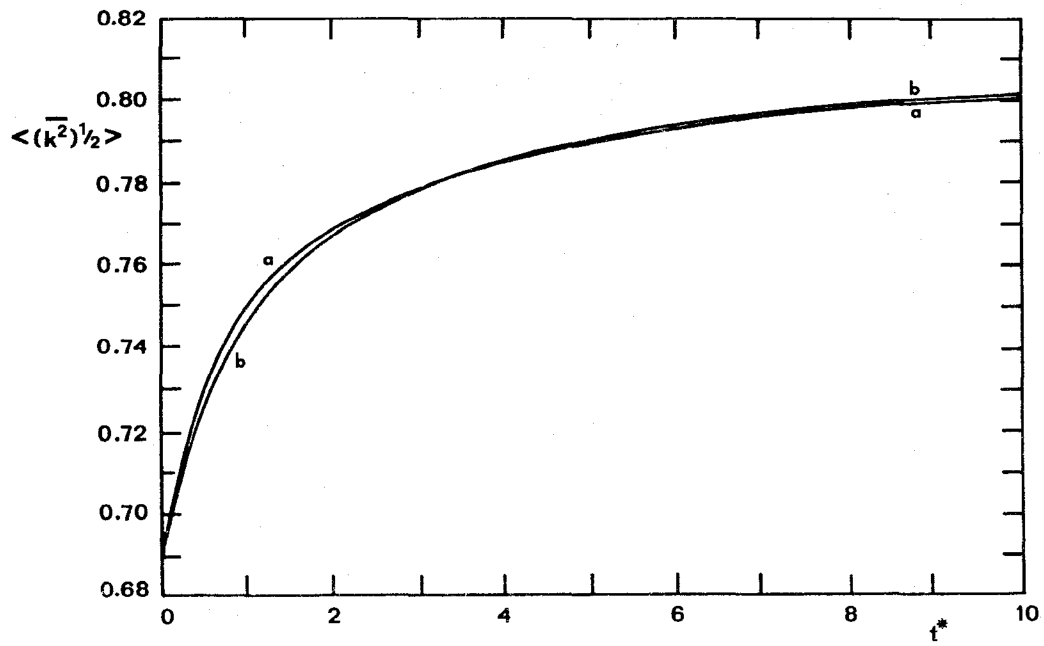

FIG. 6. Comparison between the $\langle(\overline{\kappa^2})^{1/2}\rangle$ computed by simulation (a) and that obtained with Eq. 4.2 (b) for $q = 1$.

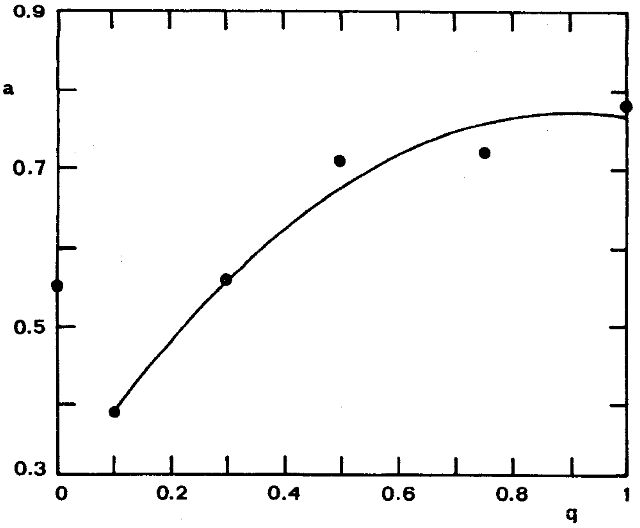

FIG. 7. Fitting parameter [Eq. (4.2)] as a function of the relative mobility q. The fitting polynomial, Eq. (4.3), is shown by a solid line.

With the time span used ($t^* < 10$) no adequate treatment can be given to curves with $0 < q < 0.1$, since these hardly differ from the curve with $q = 0$. This, on the other hand, means that the curve of $q = 0$ can be used for $q < 0.1$ if the time scale of interest is less than τ_r/q, i.e., whenever the slower molecule is essentially immobile.

If the time scale of interest is much larger than τ_r, but comparable to τ_r/q, then the faster molecule may be considered to be in the dynamic limit, and in this scale, $\langle(\overline{\kappa^2})^{1/2}\rangle$ will appear to evolve from 0.7968... [Eq. (2.34)] to 0.8164..., Eq. (2.29), since then (see Appendix A)

$$\langle(\overline{\kappa^2})^{1/2}\rangle = \langle(\overline{\cos^2\theta} + 1/3)^{1/2}\rangle. \qquad (4.4)$$

This time evolution can be computed in a manner quite analogous to that used in the simulation procedure described in Sec. III. Owing to the small difference between the two dynamical limits it was not deemed worthwhile to perform the computation. As a first approximation, Eq. (4.3) may be used for $q < 0.1$, since it extrapolates well to $q = 0$, i.e., fits well the curve with $q = 0$ when $y_\infty = (2/3)^{1/2}$ is used.

V. SUMMARY AND CONCLUSIONS

The effect of molecular reorientation on direct energy transfer was investigated. For this purpose, a Monte Carlo simulation was carried out within the isotropic diffusion model. In the three-dimensional case, the orientational dependence of the decay law is contained in the time-dependent factor $\langle(\overline{\kappa^2})^{1/2}\rangle$ (Eq. 2.26). This time dependence was captured in a simple, one parameter formula, Eq. (4.2). It is also concluded that the usual dynamic limit is only attained when both donor and acceptor are mobile. If one of the partners does not rotate, a second, slightly lower dynamic limit is verified.

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APPENDIX A: DERIVATION OF EQ. (2.33)

If only the acceptor is mobile, the ensemble average of Eq. (2.15) is

$$\overline{\kappa^2} = \cos^2\theta + 1/3. \qquad (A1)$$

This average has to be performed with respect to the acceptor and not to the donor, given that rotation of the acceptor changes only ω, while rotation of the donor affects both θ and ω.

Equation (2.14) displays a complete symmetry regarding donor and acceptor. This means that use of the asymmetric form, Eq. (2.15), gives at the end a result independent of having specifically considered the acceptor as the mobile partner.

$\cos\theta$ is uniformly distributed, hence use of the transformation formula[19] relating the distribution $Q(y)$ of $y = f(x)$ with the distribution of $x, P(x)$,

$$Q(y) = \int_{-\infty}^{\infty} P(x)\delta[y - f(x)]dx. \qquad (A2)$$

Yields, with $x = \cos\theta$ and $y = \kappa^2$,

$$Q(y) = \int_{-1}^{1} \frac{1}{2}\delta\left(y - \frac{3x^2+1}{3}\right)dx, \qquad (A3)$$

or

$$Q(y) = \int_{1/3}^{4/3} \frac{1}{2}(z - 1/3)^{-1/2}\delta(y - z)dz. \qquad (A4)$$

The last integral is nonzero only for $y\epsilon[1/3,4/3]$ where its value is $(y - 1/3)^{-1/2}/2$.

APPENDIX B: THE RANDOM NUMBER GENERATOR

The unit interval, pseudorandom number generator used was based on the multiplicative generator,

$$X_{i+1} = aX_i (\text{mod } m), \qquad (B1)$$

i.e., X_{i+1} is the remainder of the division of aX_i by m. Pseudorandom numbers with uniform distribution between 0 and 1 are given by

$$U_i = X_i/m. \qquad (B2)$$

Input values X_0 (seeds) were always odd integers not divisible by 5 like 777 777; Also the multiplier a used (100 011) and the modulus m used (10^{10}) were selected according to the recommendations given by Rubinstein.[20]

The shuffling procedure described in Ref. 21 was applied to the generator in order to reduce its sequencial correlation. For this purpose, successive values of U were stored randomly in a vector with 100 elements. After filling the vector with U_{101} to U_{200} (the first 100 U's were discarded), the shuffling procedure is started: the value of U_{201} is used to select a certain element of the vector. This element becomes the first random number to be used in the simulation, R_1. To refill the hole left behind, the next number of the primary generator, U_{202}, is stored in that position. The cycle is then repeated, with R_1 used to select the vector position to be occupied by U_{203}, etc.

APPENDIX C: DERIVATION OF EQ. (3.5)

In each jump, the original position undergoes an angular displacement α in a random direction. The angle α is related to the angle θ between the rotation axis and the point direction, and to the angle of rotation around the axis, δ (a fixed quantity) by

$$\cos\alpha = \cos\delta + (1-\cos\delta)\cos^2\theta. \tag{C1}$$

Since the rotation axis is random, the angular distribution $f(\theta)$ is that of a random point on a sphere,

$$f(\theta) = \tfrac{1}{2}\,\mathrm{sen}\,\theta. \tag{C2}$$

The distribution of α, $g(\alpha)$, is obtained from the above equations by use of Eq. (A2). One gets

$$g(\alpha) = \frac{\mathrm{sen}\,\alpha}{2[(1-\cos\delta)(\cos\alpha-\cos\delta)]^{1/2}}. \tag{C3}$$

The average $\langle\alpha^2\rangle$ is then given by

$$\langle\alpha^2\rangle = \int_0^\delta 2\alpha\left(\frac{\cos\alpha-\cos\delta}{1-\cos\delta}\right)^{1/2} d\alpha. \tag{C4}$$

For small δ, Eq. (C4) reduces to

$$\langle\alpha^2\rangle = \tfrac{2}{3}\delta^2. \tag{C5}$$

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