

## Some Concepts in Condensed Phase Chemical Kinetics

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Some concepts in condensed phase chemical kinetics which have emerged from a recent rigorous statistical mechanical treatment of condensed phase chemical reaction dynamics [S. A. Adelman, *Adv. Chem. Phys.* **53**:61 (1983)] are discussed in simple physical terms.

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**KEY WORDS:** Condensed phase chemical kinetics.

### 1. INTRODUCTION

Many-body problems complicate the theoretical treatment of the dynamics of chemical processes occurring in solid state,<sup>(1)</sup> liquid state,<sup>(2)</sup> electrochemical,<sup>(3)</sup> and biological environments.<sup>(4)</sup>

These problems may of course be successfully attacked by full-scale molecular dynamics simulation.<sup>(5)</sup> There exist, however, general features of the condensed phase reaction problem which, if exploited, can lead to significant simplifications.

These simplifications are both calculational and conceptual. From the calculational standpoint reactive trajectories may be realistically constructed as solutions of effective few-body stochastic equations of motion. These reduced equations are of substantially smaller dimension than the corresponding equations of full molecular dynamics. How these calculational reductions may be accomplished has been described in detail elsewhere<sup>(6)</sup> and selected results of such stochastic dynamics simulations will be discussed in Sections 2 and 3.

Thus I will focus in this talk on conceptual simplifications. These may be developed from the same underlying physical features. These sim-

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plifications permit one, for example, to interpret the solvent dependence of widely occurring liquid state processes like photolytic cage escape,<sup>(7)</sup> vibrational energy relaxation,<sup>(8)</sup> and activated barrier crossing<sup>(9)</sup> in terms of changes in solvent cage equilibrium structure. The conceptual simplifications may be rigorously derived from a detailed statistical mechanical theory of condensed phase chemical dynamics, presented elsewhere.<sup>(6)</sup> I will restrict myself here, however, to a brief heuristic development of the simplifications.

The conceptual simplifications are developed in Section 2. Some computational examples which illustrate the concepts are presented in Section 3.

## 2. CONCEPTUAL BACKGROUND

The simplifications derive from the fact that condensed phase effects on reagent dynamics are dominated by the direct interactions of the reagents with their nearest neighbors in the condensed phase environment. The indirect second-nearest-neighbor interactions are less important. The still more indirect third-nearest-neighbor interactions are even less important, etc. (For systems in which long range forces are important this statement must be modified.)

This physical feature suggests the following rough strategy for simplifying many-body problems. To obtain a qualitatively realistic description of reaction dynamics, treat the influence of only the first nearest neighbors on the reagents in detail; model the influence of the environment external to these nearest neighbors. To obtain a more precise description treat the influence of the first and second nearest neighbors in detail and model the external environment, etc.

This rough strategy has an obvious limitation. It is not strictly speaking applicable to liquids since the molecular identity of the nearest neighbors, second nearest neighbors, etc. is not fixed in liquids. This difficulty may be overcome by reformulating the nearest-neighbor strategy in the time domain. This time domain formulation, which is developed in detail elsewhere<sup>(6)</sup>, leads to an approximate treatment of the autocorrelation function  $\langle \tilde{\mathcal{F}}(t) \tilde{\mathcal{F}} \rangle$  of the fluctuating force  $\tilde{\mathcal{F}}(t)$ <sup>(6)</sup> exerted by the condensed phase environment on the reagents. The main point is that to understand the qualitative features of condensed phase influence on reaction dynamics one requires precise knowledge of  $\langle \tilde{\mathcal{F}}(t) \tilde{\mathcal{F}}(0) \rangle$  only at short times. An exact description of the detailed pattern of decay of  $\langle \tilde{\mathcal{F}}(t) \tilde{\mathcal{F}}(0) \rangle$  at long times is not required.

It is often useful to reexpress this statement in terms of the frequency spectrum (cosine transform)  $\rho_F(\omega)$  of the fluctuating force autocorrelation

function. The main point is that the short-time-scale behavior of  $\langle \tilde{\mathcal{F}}(t) \tilde{\mathcal{F}}(0) \rangle$  is determined by the low-order spectral moments of  $\rho_F(\omega)$ . Thus to understand the main features of environmental influence on reaction dynamics one requires precise knowledge of only the lowest-order moments of  $\rho_F(\omega)$ . A second key point is that these lowest-order moments are relatively simple *equilibrium* properties of the condensed phase system.

This observation permits a substantial simplification of the problem of interpreting solvent effects on liquid state reactions. For this case the lowest-order moments depend on the *equilibrium* solvent density in the vicinity of the reacting solute atoms. Thus to understand the qualitative features of solvent influence on reaction dynamics one requires detailed knowledge of the local solvent structure but *not* of the local solvent dynamics.

Within the Kirkwood superposition approximation, the equilibrium local solvent density may be constructed from solute-solvent pair correlation functions  $g(r)$  as described elsewhere.<sup>(6)</sup> Thus the solvent dependence of the rates may be interpreted in terms of changes in local solvent structure as approximately measured by changes in the pair correlation functions.

To be more specific, we have found elsewhere<sup>(6,10)</sup> by detailed simulation that only the zeroth and second moments of  $\rho_F(\omega)$  are required to obtain a qualitatively realistic description of the condensed phase effect on prototypical solid<sup>(10)</sup> and liquid<sup>(11)</sup> state processes. These moments are proportional to the *equilibrium* properties  $\langle \tilde{\mathcal{F}}^2 \rangle$  and  $\langle \dot{\tilde{\mathcal{F}}}^2 \rangle$ . Thus a model for  $\langle \tilde{\mathcal{F}}(t) \tilde{\mathcal{F}}(0) \rangle$  which exactly reproduces the short-time-scale expansion

$$\langle \tilde{\mathcal{F}}(t) \tilde{\mathcal{F}}(0) \rangle = \langle \tilde{\mathcal{F}}^2 \rangle - \frac{1}{2} \langle \dot{\tilde{\mathcal{F}}}^2 \rangle t^2 + \dots \quad (1.1)$$

to order  $t^2$  and which decays to zero as  $t \rightarrow \infty$  is sufficient to realistically describe condensed phase influence in these simple systems. These criteria for monatomic solvents are conveniently fulfilled by the following Gaussian model<sup>(6,10)</sup> for the fluctuating force autocorrelation function

$$\langle \tilde{\mathcal{F}}(t) \tilde{\mathcal{F}}(0) \rangle = \langle \tilde{\mathcal{F}}^2 \rangle \exp\left(-\frac{1}{2} \frac{\langle \dot{\tilde{\mathcal{F}}}^2 \rangle}{\langle \tilde{\mathcal{F}}^2 \rangle} t^2\right) \quad (1.2)$$

I will next briefly indicate how the above concepts permit one to interpret condensed phase effects on thermal rate constants. For simplicity, I will discuss the prototype case of vibrational energy relaxation in monatomic liquids. The basic principles are, however, generalizable to more complex cases.

While the interpretation of condensed phase effects on detailed reagent dynamics is clearest in the time domain, the interpretation of these effects

on thermal rate constants is often facilitated if one moves to a frequency domain description.

This is because the efficiency of dissipation of reagent energy into the solvent depends in an extremely sensitive manner on the extent of resonance overlap between reagent frequencies relevant to the process of interest and on the frequency spectrum  $\rho_F(\omega)$ . (See Figs. 1–4 of Section 3 for an illustration of this principle.)

Thus, for example, the rate of liquid state vibrational energy relaxation of a solute normal mode with liquid state frequency  $\omega_0$  increases rapidly with the magnitude of  $\rho_F(\omega_0)$ .

Within the Gaussian model of Eq. (1.2) the frequency spectrum takes the form

$$\rho_F(\omega) = \langle \tilde{\mathcal{F}}^2 \rangle \left( \frac{2\langle \tilde{\mathcal{F}}^2 \rangle}{\pi \langle \dot{\tilde{\mathcal{F}}}^2 \rangle} \right)^{1/2} \exp \left( -\frac{1}{2} \frac{\langle \tilde{\mathcal{F}}^2 \rangle}{\langle \dot{\tilde{\mathcal{F}}} \rangle} \omega^2 \right) \quad (1.3)$$

One may show<sup>(12)</sup> the Gaussian frequency spectrum, modified to include a correction from the “tail” of  $\langle \tilde{\mathcal{F}}(t) \tilde{\mathcal{F}}(0) \rangle$ , is exact as  $\omega \rightarrow \infty$  for monatomic solvents. Since the solute vibrational frequency  $\omega_0$  typically overlaps the wings of the spectrum  $\rho_F(\omega)$  for monatomic solvents, the modified Gaussian model may be used with little error even if the true frequency spectrum is complex except in the wings.

The preceding discussion may be succinctly summarized as follows. To realistically describe the condensed phase effect on reagent trajectories one requires precise information about  $\langle \tilde{\mathcal{F}}(t) \tilde{\mathcal{F}}(0) \rangle$  only at short times. To realistically describe the condensed phase effect on reagent rate constants one often requires precise information about  $\rho_F(\omega)$  only at high frequencies. Because of these simplifications, the solvent variation of both trajectories and rate constants may be understood in terms of changes in local equilibrium solvent structure.

I next want to shift the focus slightly and describe in more detail how the equilibrium solvent cage actually influences reaction dynamics. The brief discussion of vibrational energy relaxation in liquids just provided indicates that energy dissipation effects play a basic role in condensed phase kinetics.

To obtain a complete understanding of the condensed phase effect on reaction dynamics one must also consider cage effects. It is the interplay between cage and dissipation effects which give condensed phase reagent motion its unique qualitative character. I will next discuss the distinction between cage and dissipation effects for the case of liquid state processes. With slight modification the discussion may be extended to solid state chemical phenomena.

The theoretical basis<sup>(6)</sup> for separating condensed phase effects into cage and dissipation contributions lies in the fact that the *average* solvent force exerted on the reagents may be decomposed into three distinct contributions. These are as follows:

## 2.1. The Mean Force $\langle \mathcal{F} \rangle$

The mean force is the average solvent force exerted on *infinitely slowly moving* reagents. For this hypothetical case, the average local solvent density can perfectly follow the solute motion. If only the mean force were present, the reagents would execute gas-phase-like trajectories but on a potential energy surface modified for liquid state effects.

Real condensed phase trajectories, however, differ profoundly<sup>(6,10)</sup> from gas phase trajectories because of the instantaneous and delayed cage restoring forces. These correct for the fact that the average local solvent density cannot perfectly follow the reagents moving at a finite rate.

We next discuss the instantaneous and delayed cage restoring forces.

## 2.2. The Instantaneous Cage Restoring Force

The cage effect contribution to solvent influence is governed by the instantaneous cage restoring force. While this force is a general feature of condensed phase motion (it importantly influences, for example, activated barrier crossing<sup>(10)</sup>), its nature is most easily explained in the context of photolytic cage escape. We will consider as a prototypical example iodine photolysis in simple solvents (see Figs. 5 and 6 of Section 3).

The iodine molecule is photoexcited from the ground  $X$  state and makes a Franck–Condon transition and eventually arrives on. The iodine atoms then separate with a relative velocity  $v$ . If  $v$  is sufficiently large the iodine atoms hit the solvent cage and rebound before the cage has time to relax in response to the displacement of the atoms from equilibrium. The instantaneous cage restoring force is the force responsible for this rebound.

The instantaneous cage restoring force is proportional to  $\langle \mathcal{F}^2 \rangle$ . Thus, as expected, it depends on the shortest time scale aspects of the dynamic solvent response. It is often convenient to characterize the strength of the instantaneous cage restoring force by the magnitude of a cage oscillation frequency  $\omega_{e_0}$  defined elsewhere.<sup>(6)</sup> The cage oscillation frequency is proportional to  $[\langle \mathcal{F}^2 \rangle]^{1/2}$ .

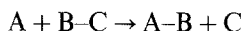
### 2.3. The Delayed Cage Restoring Force

The dissipative solvent effects are governed by the delayed cage restoring force. The nature of this force is easy to understand.

Briefly stated, if the solvent cage were rigid it would exert a conservative force on the solute which is a superposition of the mean force and the instantaneous cage restoring force. The delayed cage restoring force corrects this conservative force for the effects of cage relaxation. It thus accounts for the effects of cage nonrigidity and hence reagent-solvent energy exchange.

I next want to briefly and qualitatively indicate how the interplay between cage effects and dissipation effects influence reaction dynamics in liquids. Detailed discussions of this interplay are given elsewhere<sup>(10,11)</sup> in the context of stochastic dynamics simulations. A synopsis of some of these simulations, which amplifies the present discussion, is given in Section 3. Analytical treatments of thermal rate constants based on these same ideas will shortly be presented elsewhere.

Most adiabatic liquid state chemical reactions may be conceptually decomposed into no more than three elementary processes. Consider, for example, the liquid state atom transfer reaction



Once the commonly caged encounter complex  $AB-C$  is formed via "squeeze-out" of solvent molecules the reaction may be decomposed into three elementary processes as follows.

(i) An activated barrier crossing of the commonly caged complex taking it from the  $AB-C$  reactant state to a commonly caged vibrationally "hot"  $A-B^*C$  product state.

(ii) Commonly cage breakup to form a solvent separated  $A-B^* + C$  product state.

(iii) Vibrational thermalization of the "hot" product  $A-B^*$  to form a stabilized product  $A-B$ .

The common cage breakup process (step ii) is ultrafast and is thus cage effect dominated. That is the breakout probability is strongly dependent on the cage oscillation frequency  $\omega_{e_0}$  but only weakly dependent on detailed form of  $\rho_F(\omega)$ .

The vibrational thermalization process (step iii) is dissipation dominated. That is, as indicated above, the rate of vibrational thermalization is strongly dependent on  $\rho_F(\omega_0)$ . Cage effects do, however, play a role since the liquid state vibrational frequency  $\omega_0$  is the sum of a contribution from the mean force  $\langle F \rangle$  and a contribution from the instantaneous cage restoring force.

The activated barrier crossing process (step *i*) involves a subtle interplay between cage and dissipation effects. This interplay has been described in detail elsewhere<sup>(11)</sup>. Briefly stated, the cage effect enters because the barrier crossing step  $AB-C \rightarrow A-BC$  may be reversed in the following manner. Immediately after barrier crossing newly formed hot C can rebound off the cage and recollide with nascent product A-B to reform A-BC. The importance of this "whipback" effect increases with the magnitude of the cage oscillation frequency  $\omega_{e_0}$ . The dissipation effect enters through a mechanism similar to the familiar Kramers mechanism.<sup>(13)</sup> In the Kramers theory, however, dissipation is described by the reaction coordinate friction coefficient which is proportional to  $\rho_F(\omega=0)$ . In the treatment presented elsewhere dissipation is described by  $\rho_F(\omega)$  evaluated at a frequency which is characteristic of reaction coordinate motion in the liquid.

In order to provide concrete illustrations of the concepts discussed in this section, we next present a synopsis of stochastic dynamics studies of the cage breakup and vibrational thermalization elementary processes.<sup>(11)</sup> An analogous study of the activated barrier crossing elementary process which emphasizes the interplay between reaction coordinate "whipback" and frequency-dependent dissipation is available elsewhere.<sup>(10)</sup>

### 3. IODINE PHOTODISSOCIATION-RECOMBINATION IN SIMPLE SOLVENTS

In order to study the vibrational thermalization and cage escape processes, I next present some results of a stochastic dynamics study<sup>(12)</sup> of the photodissociation and subsequent geminate recombination of molecular iodine present at infinite dilution in model Lennard-Jones solvents.

To illustrate the concepts discussed in Section 2, I will compare stochastic dynamics studies which are based on a generalized Langevin equation of motion<sup>(6)</sup> which realistically describes short-time-scale dynamics with corresponding Langevin equation stochastic dynamics results. The Langevin equation is based on the assumption that the fluctuating force autocorrelation function is  $\delta$  correlated [cf. Eq. (1.2)] or that equivalently the spectrum  $\rho_F(\omega)$  is independent of frequency [cf. Eq. (1.3)]. Thus the chemically important short-time-scale and high-frequency dynamics are not realistically described by the Langevin model.

The details of the systems, simulation methods, and numerical methods for constructing the stochastic equations of motion have been discussed in detail elsewhere.<sup>(11)</sup> Thus I will pass directly to the results.

### 3.1. Vibrational Thermalization of Nascent $I_2$ Products

I will first discuss the liquid state vibrational thermalization of nascent  $I_2$  products formed near the dissociation limit of the ground  $X$  state. Vibrational thermalization profiles computed for a model Lennard-Jones solvent designed to simulate liquid carbon tetrachloride are plotted in Figs. 1 and 2. Figure 1 presents results based on the stochastic equation of motion<sup>(6)</sup> which realistically describes short-time-scale dynamics and Fig. 2 presents corresponding results based on a Langevin equation of motion. Plotted is the probability  $P[V, t]$  that an iodine molecule is in vibrational state  $V$  at time  $t$  conditional that it is in a state  $V \cong 95$  at  $t = 0$ .

The results of Fig. 1 show a rapid picosecond time scale relaxation to  $V \cong 60$ . Relaxation then "stagnates." Vibrational thermalization is estimated to occur on a much longer than picosecond timescale. The Langevin model results of Fig. 2 are qualitatively different. These show no "stagnation" effect but rather predict picosecond time scale thermalization of vibrational energy.

These results are readily understood using the concepts introduced in Section 2 if one additionally accounts for the fact that the effective vibrational frequency of the iodine molecule depends on its vibrational quantum number  $V$ , i.e.,  $\omega_0 = \omega_0(V)$ .

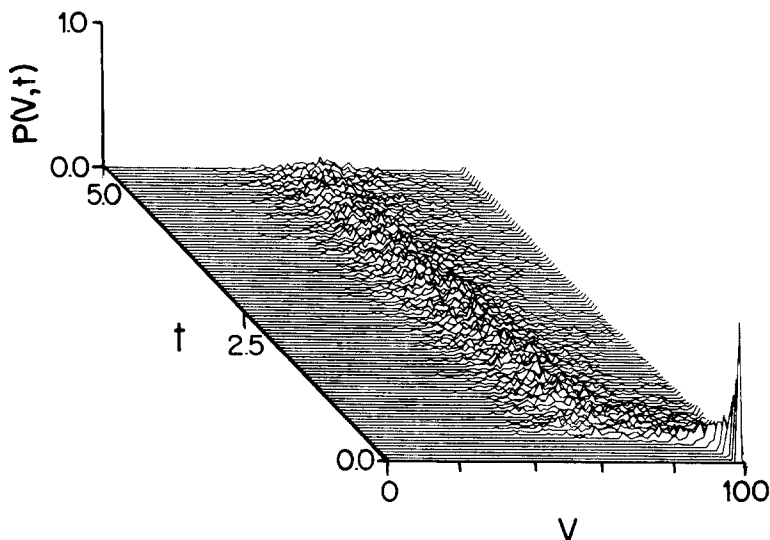


Fig. 1. Probability  $P[V, t]$  that recombining  $I_2$  molecules are in vibrational state  $V$  at time  $t$  in psec for model carbon tetrachloride solvent according to realistic stochastic dynamics.



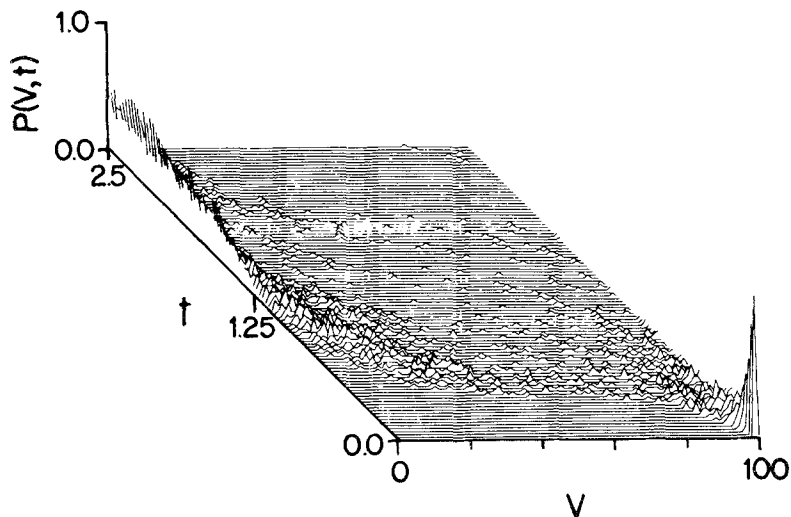


Fig. 2. Same as Fig. 1 except for Langevin stochastic dynamics.

As the iodine molecule relaxes vibrationally the effective frequency  $\omega_0(V)$  increases from small values near  $V=95$  to the fundamental  $V=0$  value of  $215\text{ cm}^{-1}$ . Because of the Gaussian fall-off of the realistic  $\rho_F(\omega)$ , Eq. (1.3), relaxation “stagnates” when  $\omega_0(V)$  becomes substantially greater than the width of the frequency spectrum  $[\langle \tilde{\mathcal{F}}^2 \rangle / \langle \tilde{\mathcal{F}}_2 \rangle]^{1/2}$  and thus has only a small overlap with  $\rho_F(\omega)$ . The Langevin model  $\rho_F(\omega)$ , in contrast, is independent of frequency. Hence Langevin dynamics unrealistically predicts no stagnation effect.

Since  $[\langle \tilde{\mathcal{F}}^2 \rangle / \langle \tilde{\mathcal{F}}_2 \rangle]^{1/2}$  depends on the local equilibrium solvent structure one expects the vibrational thermalization profile and, in particular, the stagnation point to be strongly solvent dependent. That this is the case may be seen from the vibrational thermalization profiles for  $\text{I}_2$  relaxation in model Lennard-Jones solvents designed to simulate liquid ethane and dense gaseous ethane. These are plotted in Figs. 3 and 4.

### 3.2. Cage Escape Dynamics of Photoexcited Molecular Iodine

We next discuss the cage escape step of the iodine photolysis process. The probability  $P[R, t]$  that the iodine atoms are at internuclear separation  $R$  at time  $t$  on the repulsive  $1u$  state is plotted in Fig. 5 for Langevin stochastic dynamics and in Fig. 6 for realistic stochastic dynamics.

Static solvent effects, i.e., arising from the mean force, are treated iden-

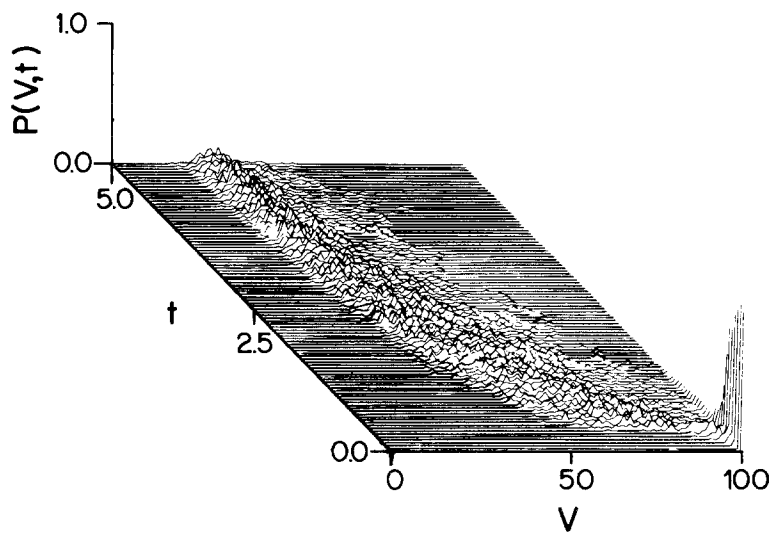


Fig. 3. Same as Fig. 1 except for liquid ethane model solvent.

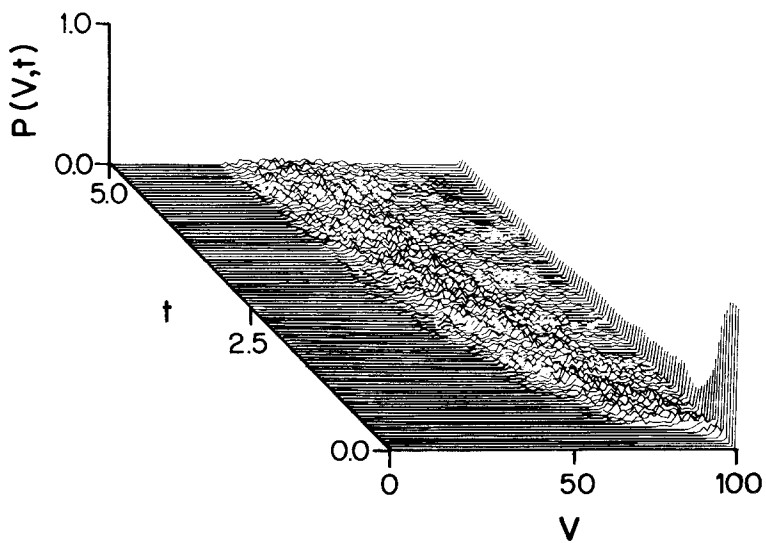


Fig. 4. Same as Fig. 1 except for dense gaseous ethane model solvent.

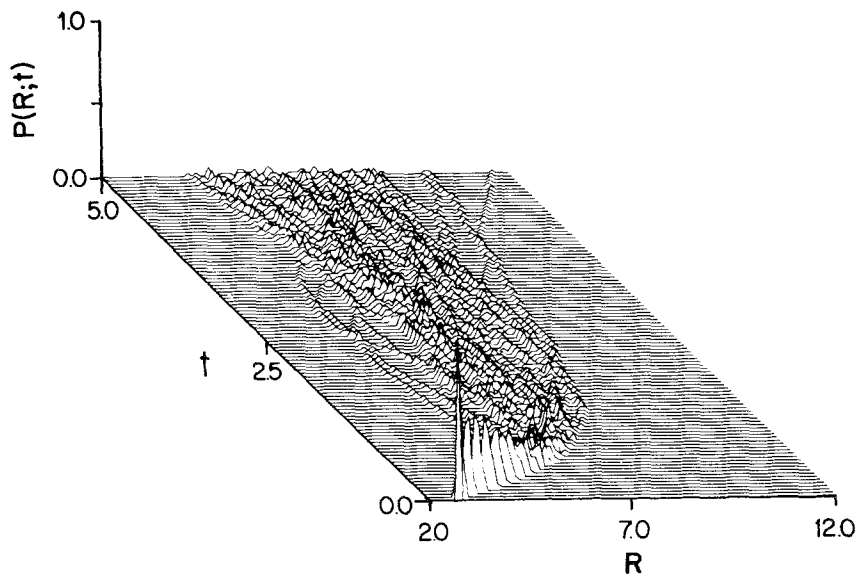


Fig. 5. Cage escape dynamics of  $I_2$  in model carbon tetrachloride solvent as calculated by Langevin stochastic dynamics.  $P[R, t]$ ,  $t$  in psec, is the probability that the iodine atoms are separated by a distance  $R$  at time  $t$  in the dissociative  $1u$  excited state.

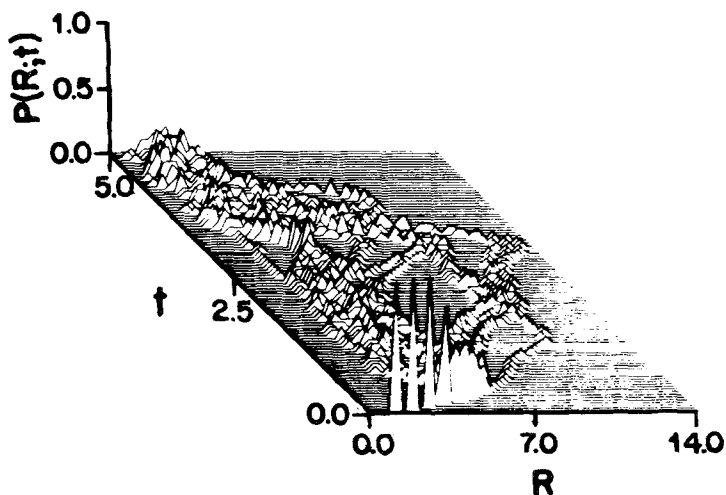


Fig. 6. Same as Fig. 5 except calculations are based on realistic stochastic dynamics as described in Ref. 11.

tically within both stochastic models. The  $1u$  potential of mean force  $W(R)$  has a slight attractive well due to liquid state packing effects. The Langevin stochastic dynamics results of Fig. 5 show that this weak static cage effect is insufficient to confine the iodine atoms to the common cage. Rather they smoothly diffuse out of the common cage.

The results of realistic stochastic dynamics show clear cage boundaries and the formation of solvent-separated iodine atoms pairs. The formation of this structure is governed by the strong instantaneous cage restoring forces  $\sim \omega_{e_0}^2$  missing in the Langevin description.

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