

ture, there is simply no effect, regardless of the value of ω .

To be more quantitative, we note that the correction factor to the conventional result for this model is $1 + kT/m\omega^2 r_0^2$, where m is the particle mass. To say that a significant correction must be a result of the smallness of ω , and not the smallness of r_0 , is a rather puzzling observation.

To support their contention that reaction path curvature is irrelevant, MNS assert that the dynamics of the process are governed by a very small region around the saddle point in the high-friction limit, whereas the curvature "by definition depends on the shape of the reaction path away from the barrier." The second statement is incorrect. Indeed, the work of LK shows that, in general, the curvature effect is determined by the radius of curvature of the lowest-energy path *at the saddle point*.

In a further attempt to justify their point of view, MNS devise a new potential energy function (to be referred to hereafter as the MNS model) which has a straight reaction path but which nonetheless gives rise to a correction to the conventional rate constant. It is easy to see that this correction has two distinct origins, namely the anharmonicity of the potential transverse to the reaction path and the spatial variation of the window frequency along this path. The LK model has neither of these features, but it still gives rise to a correction term—due to curvature. Thus, a deviation from the conventional result can have several different causes. The claim of MNS is that, since they have found a straight-path model that gives a nonzero correction, deviations from the conventional theory can *never* be ascribed to path curvature. Clearly, this conclusion cannot be justified.

Incidentally, it should be noted that the correction term related to the window frequency (as opposed to anharmonicity) in the MNS model vanishes identically if this frequency is constant, i.e., if the parameter b is zero. Once again, the smallness of ω is not enough in itself to give an effect.

In Ref. 5 it is shown that the point at which a particle is most likely to cross the separatrix between reactant and product regions may not coincide with the saddle point if the reaction path is curved. MNS confirm this, but they again claim that this shift is unrelated to the path curvature. According to their *own* analysis, however, the straight-path MNS model shows no such shift, while a shift of finite amount is found for the curved-path LK model.

Finally, it should be mentioned that the treatment of anharmonicities by MNS is inconsistent. These terms are allowed for when integrating over the barrier region [Eq. (2.18)], but they are ignored when integrating over the reactant well [Eq. (2.16)]. Thus, for a completely separable straight-path potential (say, the MNS model with $b = 0$), the MNS analysis still shows a deviation from the conventional rate constant, when in fact no such deviation can exist. It should also be noted that there is a computational error in Eq. (2.18): In the term $V^{(4)}(0)/24V^{(2)}(0)$, the 24 should be replaced by 8.

In short, the assertion of MNS that the barrier-crossing rate constant is unaffected by reaction path curvature in the high-friction limit appears to be based on faulty logic. While curvature is not the only possible cause of deviations from the conventional result, one certainly cannot say that it is irrelevant.

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Reply to "Comment on the role of reaction path curvature in diffusional barrier crossing processes"

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In the preceding Comment¹ on our recent paper,² Larson has raised again the issue of multidimensional effects in barrier-crossing dynamics. This is an important issue and we welcome the opportunity to clarify some points in our paper.² It should be made clear at the outset that our disagree-

ment with Larson concerns not the results but their interpretation.

The main point raised by Larson is that given a multiplicative correction term of the form $1 + k_B T/m\omega^2 r_0^2$ (the result for the LK model),³ in which the radius of curvature r_0

and the window frequency ω appear explicitly, our claim that the radius of curvature itself is not the essential parameter, is a "rather puzzling observation." Physically, Larson argues, the effect results from the particle deviating from its lowest energy path, bypassing the saddle point in order to reduce the overall frictional resistance. Finally, Larson says that the example brought by us to show how correction terms of the same order of magnitude are obtained in a model with a straight reaction path is irrelevant as it treats a physically different situation.

It is obvious that the Kramers reaction rate, and higher order (in $\epsilon = kT/E_B$, $E_B =$ barrier energy) corrections to it depend on the topography of the potential surface. Since the radius of curvature at the saddle point is such a topological characteristic, it should be expected that the rate can be expressed in terms of it. The fact that it appears in any rate expression is therefore not the issue [no more than the appearance of other parameters characterizing the potential at the saddle point, Eq. (2.21) of Ref. 2]. The issue is whether this fact is dynamically significant. Our answer to the negative is based on the following arguments:

(a) In the high friction limit, dynamical effects are important only at the saddle point. The shape of the reaction path away from the saddle point cannot be dynamically relevant.

(b) Path distortion in order to reduce friction is a dynamical effect. We would expect corrections of this kind to depend on the friction γ , while the LK correction and those discussed by us do not (in fact, no such corrections exist in the Smoluchowski limit because the scaling of the time with γ obtained already in the Kramers solution, is the only possible effect in this limit).

(c) In Ref. 2, we have shown that the first order corrections to the Kramers solution is associated with two factors: One is the size of the well (r_a in Fig. 2 of Ref. 2) and the other

is the shape of the potential surface at the saddle point (expressed by the window frequency and by anharmonicity parameters). We regret that even though the role of the size of the well was very clear in Sec. II of Ref. 2, it was not stressed in the conclusion to our paper. In the LK model, the dependence on r_0 comes in because r_0 characterizes the size of the reactant well. The same dependence on the well size appears also in the MNS model² [note that ω in Eq. (3.18) of Ref. 2 is the scaled frequency that should be multiplied by $(ma^2/V_0)^{-1}$ in order to get the physical frequency].

(d) It is the general result [Ref. 2, Eqs. (2.20)–(2.21)] which gives rise both to the LK result for the LK model and to the MNS result for the model (3.13) of Ref. 2. The same physical quantities—window frequency, anharmonicities at the saddle point, and the well size determine the rate in both cases.

We take this opportunity to correct some typographical errors in Ref. 2. In Eq. (2.20b) $\omega_{a_1 a_2}$ should be $\omega_{a_1} \omega_{a_2}$. In the line preceding Eq. (3.14), $\omega^2 = \omega^2 ma^2/V_0$ should be replaced by $\omega^2 = \tilde{\omega}^2 ma^2/V_0$. Also Larson is right about the shortcoming of the result (3.18); it is the correct result for a (perfectly acceptable) potential which has the form (3.13) near the saddle, but becomes harmonic deep in the well. Otherwise, additional correction terms arise from the anharmonicity of the potential in the well, which should make A independent of ω when $b \rightarrow 0$. This of course has no bearing on the issues discussed above.

Finally, we stress that we expect reaction path curvature to play an essential role in the reaction dynamics in the low friction regime, where the shape of the path away from the saddle is dynamically important.

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Comment on: X-ray diffraction study of the effects of pressure on bilayer to nonbilayer lipid membrane phase transitions

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Biological lipids exhibit complicated phase transitions as the temperature is varied.¹ Considerable work has been done on the chain-melting transition of lipids as a function of pressure as well. However, there has not been much study of the effect of pressure on the lamellar-inverted hexagonal (L_α - H_{II}) phase transition¹ that a large class of lipids, such as dioleoylphosphatidylethanolamine (DOPE), exhibit. The realization that biological systems need such nonbilayer forming lipids has made the study of bilayer to nonbilayer transitions important.

Earlier reports on the effect of pressure on the lamellar-inverted hexagonal phase transition temperature T_{BH} have been contradictory. Yager and Chang² reported that in egg-PE, pressure reversal of the transition was consistent with a value of dP/dT_{BH} of 22 bar/K. Recently, however, using FTIR spectroscopy, Wong *et al.*³ reported that a major structural phase transition occurs in aqueous dispersions of pure synthetic DOPE at room temperature only at pressures as high as 9 kbar, which they interpreted as a reversed micellar (i.e., H_{II}) to lamellar transition. The value reported by