Reply to "Comment on 'Quasisaddles as relevant points of the potential energy surface in the dynamics of supercooled liquids'" [J. Chem. Phys. 118, 5263 (2002)]

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The criticisms made by Doye and Wales concern the fact that we call the local minima of $W=|\nabla V|^2$ "quasisaddles,"[1] to suggest a relationship between them and the true saddles (absolute minima of W with $W=0$). In reanalyzing their large database[2] of nonstationary points (quasisaddles in our notation, QSPs) they show that the large majority of the QSPs has only one zero Hessian eigenvalue, instead of a number between one and four (as we found in our analysis reported in Ref. 1 with a lower numerical precision). We appreciate the Doye and Wales improvement of the statistic, but we do not feel that, aiming to understand the dynamics of supercooled liquids and the role of QSP, "less than four" is different from "just one." In other words, while we learn with interest that the better precision reported in the Doye and Wales Comment allows us to establish that the QSPs have one and only one nonzero gradient direction, we do not think this leads to a new interpretation of our results. Indeed, the main concept we based our analysis on was the fact that at quasisaddle points the ∇V is very small, so they are points on the landscape where dynamics slow down significantly. The fact that the forces are very small and the number of zero curvatures (excluding the zeros associated to global continuous symmetries, i.e., translations) are very few—from one to four in our previous analysis, and exactly one in the refined computation of Doye and Wales—led us to "conjecture" that the dynamical properties of the system in proximity of quasisaddles are very similar to those of true saddles, for which the forces and the number of zero curvatures are both exactly zero. For this reason we have used the term "quasisaddles." To better clarify our thinking: (i) it is trivial that the QSPs do not have the mathematical properties of a saddle (otherwise we would have called them saddles), and (ii) QSPs share with true saddles the fact that W is more than 8 orders of magnitude smaller than the value of W at equilibrium. Therefore the slow dynamics is controlled by QSPs, in a similar manner as by true saddles. The statement of Doye and Wales that "any point in configuration space is a stationary point in the subspace orthogonal to the gradient" is correct but it does not take into account the fact that a quasisaddle has the further property to have a small value of the gradient of V—an essential feature for our hypothesized relationship between them and true saddles.

As a further numerical indication supporting our conjecture on the similarity between quasisaddles and true saddles as far as the dynamical properties are concerned, we report in Fig. 1 the temperature dependence of the order (fractional number of negative eigenvalues of the Hessian) of both quasisaddles and true saddles for binary mixture Lennard-Jones[3,4] with $N=256$. The true saddles are recognized by their very low value of W, which is about 10 orders of magnitude less than that of quasisaddles. Even if the statistics of quasisaddles is better (they are sampled very often, about 50 times more than true saddles), we observe a clear coincidence of the two set of data, strongly supporting our hypothesis that quasisaddle properties are a good approximation of saddle ones. Both data extrapolate to zero at the same temperature, that coincides with the mode-coupling temperature $T_{MCT}=0.435$ (indicated by an arrow in the figure). Our

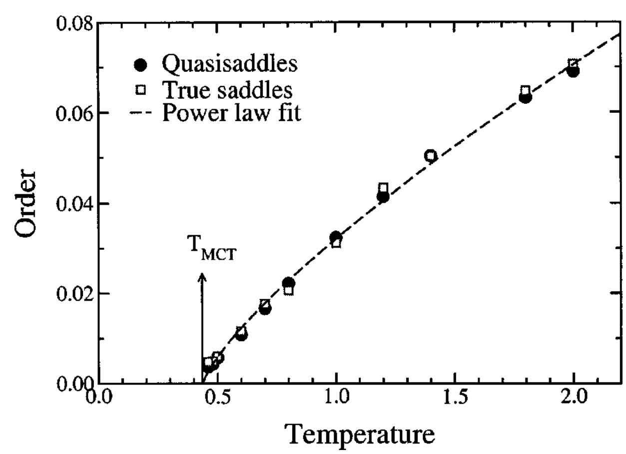

FIG. 1. Temperature dependence of fractional order of quasisaddles (full circles) and true saddles (open squares). The dashed line is a power law fit and T_{MCT} is the mode-coupling temperature for the binary mixture Lennard-Jones model analyzed.

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finding then suggests that, no matter if they are quasi or true saddles, the minima of W bring the relevant information about the slow dynamics taking place in supercooled liquids, allowing a landscape interpretation of the observed slowing down approaching T_{MCT}.[1,3]

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