

Some Further Results for the Stationary Points and Dynamics of Supercooled Liquids

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Abstract

We present some new theoretical and computational results for the stationary points of bulk systems. First we demonstrate how the potential energy surface can be partitioned into catchment basins associated with every stationary point using a combination of Newton-Raphson and eigenvector-following techniques. Numerical results are presented for a 256-atom supercell representation of a binary Lennard-Jones system. We then derive analytical formulae for the number of stationary points as a function of both system size and the Hessian index, using a framework based upon weakly interacting subsystems. This analysis reveals a simple relation between the total number of stationary points, the number of local minima, and the number of transition states connected on average to each minimum. Finally we calculate two measures of localisation for the displacements corresponding to Hessian eigenvectors in samples of stationary points obtained from the Newton-Raphson-based geometry optimisation scheme. Systematic differences are found between the properties of eigenvectors corresponding to positive and negative Hessian eigenvalues, and localised character is most pronounced for stationary points with low values of the Hessian index.

1 Introduction

Stationary points of a potential energy surface, V , correspond to structures where the gradient of the potential vanishes, while the Hessian index, I , is defined as the number of negative Hessian eigenvalues. Stationary points with $I \geq 1$ are often referred to as saddles. A number of studies have recently focused upon the properties of saddle points for model supercooled liquids and glasses.^{1,2,3} A rigorous partitioning of the potential energy surface is possible in terms of the catchment basins of local minima [often termed ‘inherent structures’ for bulk material^{4,5}] using steepest-descent paths. The superposition approach to thermodynamics, where the total partition function is written as a sum over local minima, follows naturally from this scheme.^{6,7,8,9,10,11,12} Dynamical properties can also be calculated within this framework if minimum-to-minimum rate constants are available, using master equation,^{13,14} kinetic Monte Carlo,^{15,16,17,18} or discrete path sampling¹⁹ techniques. These schemes generally consider only local minima and true transition states, i.e. stationary points with Hessian index one (a single negative eigenvalue) in view of the Murrell-Laidler theorem,²⁰ which states that if two minima are connected by an index two saddle, then there must be a lower energy path between them involving only true transition states.

The potential energy surface itself is independent of temperature, atomic masses and the coordinate system. Direct analysis of V itself has revealed connections between the global properties of the surface and the interparticle forces,²¹ as well as a theoretical basis for the empirical result^{22,23} that the number of different local minima increases exponentially with size.^{6,7,24,25} The distribution of minima as a function of the potential energy can also be found from simulation data,^{26,12} and

this approach has now been used in several studies of bulk material.^{27, 28, 29, 30, 31, 32, 33, 34, 35, 11, 36, 37} An approximately Gaussian form is expected for sufficiently large systems.^{38, 39, 40, 25} Distributions of transition states and barrier heights have also been reported for bulk models.^{41, 42, 43, 44}

Proposals to extend such ideas to consider a partition of configuration space in terms of saddle points have been suggested in the context of supercooled liquids and glasses.³ This approach has much in common with the instantaneous normal mode theory developed by Keyes and coworkers,^{45, 46, 47} where the focus of attention is the spectrum of Hessian eigenvalues for instantaneous configurations. Theoretical contributions based upon the premise of dividing configuration space into saddles have appeared,^{48, 49, 50, 51} following the observation that the Hessian index of the stationary points sampled in simulations approaches zero around the critical temperature of mode-coupling theory.^{1, 2, 52, 53, 54, 55, 56, 57, 58, 59, 60} However, in contrast with the partitioning scheme based upon local minima, a well-defined procedure for using other stationary points in this way has yet to be fully developed. In particular, the most common mapping used is the minimisation of the square gradient, $|\nabla V|^2$,⁶¹ but this tends not to produce true stationary points for large systems, as we have explained in a previous contribution.²⁵ In §2 we show how an alternative approach based upon Newton-Raphson and eigenvector-following techniques can be used to achieve the desired partitioning.

A further development of the present work is the analysis of stationary points for bulk models in terms of independent subsystems. In §3 we first present analytic solutions for the combinatorial problem that determines the number of stationary points of Hessian index I in a system containing N atoms. These results complement recent theoretical developments of Keyes and coworkers^{62, 63} based upon a random energy model approach,^{64, 65, 66, 67} and should be useful in future studies that consider the dynamics and thermodynamics of model systems.⁶⁸ We then consider the validity of the independent subsystem approximation by examining properties of the Hessian eigenvectors for the samples of stationary points reported in §2.

Since saddles beyond index one usually make no significant contribution to the dynamics of small molecules it is important to demonstrate that conventional dynamical approaches are not incompatible with sampling of higher index saddles in simulations. Just as most of the volume of a hypersphere is associated with the surface when the dimension becomes high enough,⁶⁹ most of the configuration space in a large system must lie near the surface of the catchment basins for the local minima.⁷⁰ This observation does not invalidate the partition of configuration space into the basins of attraction of local minima. Nevertheless it has been suggested that as the temperature increases the dynamics of a supercooled liquid might be interpreted in terms of transitions between configuration space associated with saddles, rather than between local minima.^{1, 2, 52, 53, 54} Such a partitioning is now technically feasible, as shown in §2, but it is not yet clear whether it offers any advantages over the simpler approach based on minima and true transition states.

2 A New Partitioning Scheme

In this section we describe a partitioning scheme that divides the potential energy surface into regions associated with each stationary point. Numerical results have been obtained for the same binary Lennard-Jones system of 256 atoms (205 A and 51 B) as we considered in earlier work,²⁵ and further details of the model can be found in that publication. Qualitative changes in behaviour for various properties have previously been reported for this system around the mode-coupling theory critical temperature of $T_c \approx 0.435$, as mentioned above.

In addition to the new searches described below, all the molecular dynamics (MD) and geometry optimisations were repeated for the 256-atom system to correct a systematic problem that affected the results in our previous report.²⁵ The present results therefore supersede those in the latter paper, although none of the conclusions in the previous contribution are affected. As before,

every 1000th configuration from the data collection phase was saved and used as a starting point for the following geometry optimisations: (1) minimisation using Nocedal’s LBFGS algorithm,⁷¹ (2) a transition state search using hybrid eigenvector-following,^{72,10,73} (3) minimisation of $|\nabla V|^2$ using Nocedal’s LBFGS algorithm.⁷¹ The implementation of these algorithms and the convergence criteria were the same as in previous work.²⁵ The new geometry optimisations in the present work are based upon a combination of Newton-Raphson-type steps and eigenvector-following. The step along eigendirection α in the Newton-Raphson-type search was taken as^{74,10}

$$x_\alpha = \frac{-2g_\alpha}{\varepsilon_\alpha^2(1 + \sqrt{1 + 4g_\alpha^2/\varepsilon_\alpha^4})}, \quad (1)$$

where g_α and ε_α^2 are the component of the gradient and Hessian eigenvalue corresponding to eigenvector α , respectively. The sign of ε^2 determines whether the step in direction α raises or lowers the energy, and leads to the well-known result that Newton-Raphson-type geometry optimisations can converge to stationary points of any Hessian index.^{75,76,12} In the present case this is precisely the behaviour that we require, and each Newton-Raphson-type optimisation therefore began with a maximum of twenty such steps in combination with a dynamic trust radius scheme for the maximum step size.^{77,78,74} Some of these initial geometry optimisations were already converged to a root-mean-square gradient of less than $10^{-7} \epsilon_{\text{AA}}/\sigma_{\text{AA}}$. However, for configurations obtained from the higher temperature simulations the usual behaviour was for the number of negative Hessian eigenvalues to fall somewhat from the initial value and then oscillate without converging. This behaviour probably arises because the geometry optimisation does not proceed systematically uphill or downhill when the sign of an eigenvalue changes sign. We therefore employed a fixed number (twenty) of these Newton-Raphson-type steps before switching to an eigenvector-following search for a stationary point of fixed Hessian index given by the number of negative eigenvalues at the last Newton-Raphson iteration. The step now becomes

$$x_\alpha = \frac{\pm 2g_\alpha}{|\varepsilon_\alpha^2|(1 + \sqrt{1 + 4g_\alpha^2/\varepsilon_\alpha^4})}, \quad (2)$$

plus for uphill and minus for downhill, independent of the sign of ε_α^2 , and all these searches were tightly converged to stationary points of the required index. A dynamic trust radius step scaling scheme was again employed in this phase of the optimisation.

The results of these calculations are collected in Tables 1, 2 and 3. As in previous work the number of different minima and transition states sampled and the fraction of negative eigenvalues decrease markedly around T_c , but the system is only trapped in a single local minimum on the simulation time scale well below this temperature.^{42,43,25,44} Most minimisations of $|\nabla V|^2$ converge to non-stationary-points (NSP’s) rather than true stationary points (SP’s) of V , especially at higher temperature.

Statistics for the mean potential energy difference and displacement in configuration space between the starting point and the final geometry after each optimisation are collected in Table 2. While the displacements are practically the same for each class of geometry optimisation the energy differences are always ordered $\Delta V_{\text{min}} > \Delta V_{\text{ts}} > \Delta V_{\text{G2}} > \Delta V_{\text{NR}}$. By this measure the Newton-Raphson-type scheme has clearly succeeded in finding ‘closer’ stationary points to the original configurations, although the displacement statistics do not discriminate between them. This scheme also provides a true partitioning of the configuration space into regions associated with all the stationary points, although the precise boundaries will depend upon details of how the algorithms are implemented, such as the maximum step size allowed.^{75,76} In contrast, if steepest-descent paths are used to divide the space into catchment basins for local minima then the mapping is in principle unambiguous. This result follows because steepest-descent is defined in terms of a first-order differential equation, for which a uniqueness theorem applies.¹²

3 Stationary Points for Independent Subsystems

We now extend previous results^{6,7,24,25} for the number of local minima and transition states to stationary points of any Hessian index. This analysis is based upon the assumption that a sufficiently large system of mN atoms can be divided into m effectively independent subsystems of N atoms each. Writing the number of stationary points of index I in an N -atom system as $n_{\text{sp}}(N, I)$ it follows that

$$n_{\text{sp}}(mN, 0) = n_{\text{sp}}(N, 0)^m. \quad (3)$$

The solution of this equation is

$$n_{\text{sp}}(N, 0) = \exp(\alpha N), \quad (4)$$

where α is a constant.

A similar argument can be given for the number of transition states.²⁵ Assuming that the rearrangements associated with the transition states can be localised to one subcell, the whole mN -atom system will be at a transition state when one of the subsystems is at a transition state and the rest are at a minimum, so

$$n_{\text{sp}}(mN, 1) = m n_{\text{sp}}(N, 1) n_{\text{min}}(N)^{m-1}, \quad (5)$$

with solution

$$n_{\text{sp}}(N, 1) = aN \exp(\alpha N), \quad (6)$$

where a is another constant.

For index two saddles we have

$$n_{\text{sp}}(mN, 2) = m n_{\text{sp}}(N, 2) n_{\text{sp}}(N, 0)^{m-1} + \frac{m(m-1)}{2} n_{\text{sp}}(N, 1)^2 n_{\text{sp}}(N, 0)^{m-2}, \quad (7)$$

where the two terms correspond to the two ways that an index two saddle for the mN -atom system can be generated. More generally

$$n_{\text{sp}}(mN, J) = m! \sum_{\{n_0, n_1, \dots, n_J\}} \prod_{I=0}^J \frac{n_{\text{sp}}(N, I)^{n_I}}{n_I!}, \quad (8)$$

where n_I is the number of the m subsystems that are at a stationary point of index I , and the sum is over the combinations of n_I values that satisfy $\sum_I n_I = m$ and $\sum_I I n_I = J$. The $m! / \prod_{I=0}^J n_I!$ factor in the above sum is a multinomial coefficient, and the sum itself corresponds to the terms in the multinomial series expansion of

$$[n_{\text{sp}}(N, 0) + n_{\text{sp}}(N, 1) + \dots + n_{\text{sp}}(N, I_{\text{max}})]^m \quad (9)$$

with the appropriate value of J , where I_{max} is the maximum value of I for the N -atom system. This observation enables us to derive a general expression for $n_{\text{sp}}(N, I)$ by writing the multinomial as

$$\left[x^0 n_{\text{sp}}(N, 0) + x^1 n_{\text{sp}}(N, 1) + x^2 n_{\text{sp}}(N, 2) + \dots + x^{I_{\text{max}}} n_{\text{sp}}(N, I_{\text{max}}) \right]^m. \quad (10)$$

The terms contributing to $n_{\text{sp}}(mN, J)$ correspond to the coefficient of x^J , so

$$n_{\text{sp}}(mN, J) = \frac{1}{J!} \frac{d^J}{dx^J} \left[\sum_{I=0}^J x^I n_{\text{sp}}(N, I) \right]^m \bigg|_{x=0}. \quad (11)$$

We can now prove that the general solution to these equations is

$$n_{\text{sp}}(N, I) = \binom{aN}{I} \exp(\alpha N), \quad (12)$$

where the binomial coefficient

$$\binom{aN}{I} = \frac{aN!}{I!(aN-I)!} \quad \text{or} \quad \frac{\Gamma(aN+1)}{\Gamma(I+1)\Gamma(aN-I+1)!} \quad (13)$$

for integer and non-integer values of a , respectively. Substituting for $n_{\text{sp}}(N, I)$ from equation (12) gives

$$\begin{aligned} n_{\text{sp}}(mN, J) &= \frac{1}{J!} \frac{d^J}{dx^J} \left[\sum_{I=0}^J x^I \binom{aN}{I} \exp(\alpha N) \right] \Big|_{x=0}^m \\ &= \frac{1}{J!} \frac{d^J}{dx^J} (1+x)^{aN} \Big|_{x=0} \exp(\alpha mN) \\ &= \frac{J!}{J!} \binom{amN}{J} \exp(\alpha mN) = \binom{amN}{J} \exp(\alpha mN), \end{aligned} \quad (14)$$

which is consistent with the supposition of equation (12).

From equation (9) it is clear that the total number of stationary points of any index must obey

$$n_{\text{sp}}^{\text{tot}}(mN) = n_{\text{sp}}^{\text{tot}}(N)^m. \quad (15)$$

Therefore, $n_{\text{sp}}^{\text{tot}}(N)$, like $n_{\text{sp}}(N, 0)$, is a simple exponential:

$$n_{\text{sp}}^{\text{tot}}(N) = \exp(\gamma N), \quad (16)$$

where γ is a constant.

$n_{\text{sp}}^{\text{tot}}(N)$ can also be obtained from $n_{\text{sp}}(N, I)$ by summing over I :

$$n_{\text{sp}}^{\text{tot}}(N) = \exp(\alpha N) \sum_I \binom{aN}{I} = 2^{aN} \exp(\alpha N) = \exp[(\alpha + a \ln 2)N]. \quad (17)$$

Our result for $n_{\text{sp}}(N, I)$ therefore implies a relationship between the the total number of stationary points, the scaling exponent for the number of minima and the number of transition states connected on average to each minimum, which is $n_{\text{sp}}(N, 1)/n_{\text{sp}}(N, 0) = aN$. These parameters are connected by the equation

$$\gamma = \alpha + a \ln 2, \quad (18)$$

which we anticipate may play an important role in future energy landscape analysis of bulk systems. For example, the ratio between the number of transition states and the number of local minima must scale appropriately for thermodynamic and dynamic properties to exhibit proper extensive or intensive behaviour.^{62,68,63,51}

If $n_{\text{sp}}(N, I)$ has the form given in equation (12) then the probability of choosing a stationary point of index I from all the stationary points of a system containing N atoms is

$$P(N, I) = \binom{aN}{I} 2^{-aN}. \quad (19)$$

This distribution can be closely approximated by the Gaussian form

$$P(N, I) \approx \frac{e^{-(I-\mu)^2/2\sigma^2}}{\sqrt{2\pi\sigma^2}}, \quad (20)$$

with $\mu = Na/2$ and $\sigma^2 = Na/4$. Although this approximation does not give the correct scaling behaviour for $P(N, 1)/P(N, 0)$ it is quite accurate in most other respects. The difference between the tails of the two distributions occurs because the Gaussian tends to zero at $I \rightarrow \pm\infty$, whereas the binomial distribution vanishes at $I=-1$ and $aN+1$, so that $I_{\max}=aN$. The latter limit provides a physical constraint on a , namely, $a \leq d$, where d is the dimension of the system.

The above results complete our previous analysis, and are in good agreement with the Gaussian distributions found empirically for small clusters.²⁵ For the clusters the maximum of the distribution occurs at $I \approx N - 2$, and therefore $a \approx 2$. Whether this result holds for bulk systems with periodic boundary conditions is not yet clear. The value $a = 2$ may reflect the open boundary conditions for the clusters, where there must always be $N - 1$ stable modes or the cluster will dissociate.²⁵

Our results also complement the empirical observation that the average potential energy of stationary points with index I appears to scale linearly with I . A theoretical justification for the latter observation has been obtained by Shell *et al.* within a similar framework that considers independent subsystems.⁵¹ These authors employ a maximum term approximation to find the most probable saddle index, and equation (20) indicates that this should be a good approximation for large enough systems. In particular, they predict that the density of saddle points with fractional index, $i = I/dN$, should scale exponentially with size with a coefficient that depends on i , i.e. as $\exp[N\theta(i)]$. Using our expression for $n_{\text{sp}}(N, I)$ it is easy to show that

$$\theta(i) = \alpha + \frac{1}{N} \ln \left(\frac{aN}{idN} \right), \quad (21)$$

which varies between α and $\alpha + a \ln 2$ (in the limit of large N). Our derivations also complement results based on the Morse rules,⁷⁹ which can provide upper and lower bounds for the number of stationary points of a given index.^{80,81}

4 Stationary Points and Dynamics

The above analysis is based on the assumption of independent, or weakly interacting, subsystems. Previous work on finite size effects for model glass formers provides support for this picture, including the result that ‘a system of $N = 130$ particles behaves basically as two non-interacting systems of half the size’.^{30,82} In this idealised limit the procedure to calculate dynamical properties, such as the diffusion constant, D , is straightforward. For example, suppose that each subsystem consists of minima that are each connected to two neighbouring minima via two transition states. If the rate constant corresponding to each transition state is the same, and equal to k , then the expected waiting time between transitions is $1/2k$. If the minima are assumed to be arranged linearly in space, and each connected pair is separated by the same distance d , then the mean squared displacement after n steps is simply nd^2 for uncorrelated transitions. The average time for n steps to occur is $n/2k$, and so the one-dimensional diffusion constant is simply $D = kd^2$. For a weakly interacting system of m such subsystems the dimension of the configuration space is multiplied by m . The expected waiting time in any one of these higher-dimensional minima is now $1/2mk$, because there are now $2m$ transition states connected to each minimum. However, the same diffusion constant is obtained as for a single subsystem, because the displacement must be averaged over m times as many atoms.

Now suppose that we try to find the diffusion constant using a kinetic Monte Carlo approach^{15,16,17,18} and calculations of minima and transition states.⁴² In this case a statistical rate theory may be used to estimate the transition state k using the properties of the stationary points or pathways. For the single subsystem described above the average waiting time per transition is then $1/2k$, and the correct diffusion constant will be obtained so long as both transition states are located for each minimum visited. Now consider the system containing m weakly interacting copies of this subsystem. In this case it is necessary to locate $2m$ transition states per minimum, and the waiting time becomes $1/2mk$, so that much smaller time increments occur in the resulting KMC simulation. However, the correct diffusion constant should still be obtained after averaging displacements over all the subsystems.

It is clear from the above discussion that KMC simulations may become much less efficient as the system size increases if all the atoms play an active role in diffusion. At higher temperatures efficiency is not really the point, since standard MD calculations provide a straightforward route to D . Rather, the KMC approach is of interest because it provides a coarse-grained picture of the relevant processes. Sampling problems do indeed appear to be an issue for KMC simulations of glasses, as we will report elsewhere.⁸³ Nevertheless, the correct diffusion constant can in principle be obtained from such calculations by considering only local minima and true transition states, as long as the transitions are Markovian. This result is not in contradiction with the observation that progressively higher index saddles may be sampled as the temperature increases. For example, the mean Hessian index of instantaneous configurations or stationary points obtained by the geometry optimisation procedure of §2 can easily be calculated for one-dimensional double-well (Figure 1) or periodic potentials.^{58,84} The average index for m copies of such non-interacting systems would simply be m times larger. Hence the stationary points sampled by the Newton-Raphson procedure of §2 would include progressively higher index saddles as a function of temperature, up to a limiting value determined by m . It may also be significant that the index falls to zero only in the zero temperature limit, although linear extrapolation of data from the range $0.2 < kT/\epsilon < 0.5$ would suggest a non-zero value (Figure 1). Interestingly, as noted previously from simulations by Doliwa and Heuer⁸⁵ and from simple models by Berthier and Garrahan,⁸⁶ if the same data is represented on an Arrhenius plot a straight line results, arguing against a sharp transition in the properties of saddles near to the mode-coupling temperature.

It is sometimes stated that the inherent structure approach to the dynamics of supercooled liquids is only relevant in the temperature range where there is a separation of time scales for vibrational motion and transitions between minima.^{3,87,88} However, the above discussion on the system size dependence of the residence times for local minima indicates that this separation depends on system size as well as the temperature. Goldstein, in his landmark paper on the application of the potential energy landscape to the study of supercooled liquids,⁸⁹ actually argued for the separation of two *atomic* time scales. The first time scale corresponds to localised vibrations of an atom around its mean position, and the second to the time taken for a transition that involves a significant displacement of this atom. Goldstein realized that, whilst a specified atom is vibrating, many transitions could potentially occur between minima that involve rearrangements localised elsewhere in the system. In practice, the inherent structure approach to dynamics will be most useful when the times between interminimum transitions are long compared to the time scale for vibrational motion. For this reason it has been argued that the system size needs to be small enough for this time scale separation to be present.^{90,91,88,92}

The previous discussion also shows that analysis of dynamics using a configuration space partitioned into local minima and considering only true transition states is not incompatible with the system ‘sampling’ higher index saddles. However, all the arguments are based on the notion of independent subsystems, and we therefore examine how well this picture might apply to the stationary points obtained for the binary Lennard-Jones system discussed in §2 using the Newton-

Raphson-type procedure. Two distinct indices have been calculated for each of these points, as described below.

The first ‘localisation’ index, L , was defined as

$$L_{\alpha\beta} = \sum_{\gamma=1}^{3N} |c_{\gamma}^{\alpha} c_{\gamma}^{\beta}|, \quad (22)$$

where c_{γ}^{α} is component γ of normalised Hessian eigenvector α . For every stationary point with Hessian index two or higher we calculated the average value of L over the $I(I-1)/2$ pairs of eigenvectors with negative eigenvalues, L_{minus} . The statistics for stationary points of the same index were found to be very similar for samples obtained from the MD runs at different temperatures, and so averages over all the runs are presented in Figure 2. For eigenvectors corresponding to motion in different regions of space (or different atoms) we would expect $L = 0$, while for motion localised on the same atoms L should approach unity. The corresponding averages over all pairs of eigenvectors corresponding to positive eigenvalues, L_{plus} , were also calculated for comparison. Figure 2 reveals that L_{plus} is around 0.55 practically independent of the index. In contrast, L_{minus} is systematically smaller, particularly when the index is less than about ten.

We have also calculated

$$\tilde{N}_{\alpha} = \left(\sum_{\gamma} (c_{\gamma}^{\alpha})^2 \right)^2 / \sum_{\gamma} (c_{\gamma}^{\alpha})^4, \quad (23)$$

for all eigenvectors with non-zero Hessian eigenvalues. $\tilde{N}$ is proportional to the participation ratio,⁹³ and is expected to vary between one for localised modes to about N for delocalised modes. Figure 2 shows the results for modes with positive and negative eigenvalues, $\tilde{N}_{\text{plus}}$ and $\tilde{N}_{\text{minus}}$, separately for comparison, and again we display averages over stationary points from the different MD runs. Here the difference between $\tilde{N}_{\text{plus}}$ and $\tilde{N}_{\text{minus}}$ is even more marked than for L_{plus} and L_{minus} .

The statistics for both L and $\tilde{N}$ both indicate that the characteristic displacements associated with Hessian eigenvectors that have negative eigenvalues are more localised and spatially independent than for eigenvectors associated with positive eigenvalues. For both measures it is the stationary points with the fewest negative eigenvalues for which this character is most pronounced. These results appear to agree very well with the analysis of Shell *et al.*, who conclude that low-index saddles may often be described in terms of combinations of transition states of the subsystems.⁵¹

5 Conclusions

We have previously pointed out the need for rate constants and related dynamical properties, such as the diffusion constant, to scale correctly with system size.²⁵ The total energy and its fluctuations are extensive quantities, while the barrier heights between local minima and true transition states are intensive. If ‘activated’ processes are defined by comparing such extensive and intensive quantities then one would be forced to conclude that no ‘activated’ processes exist at any infinitesimal temperature in a bulk system.^{1,59} We have previously argued that such a definition is inappropriate,²⁵ since rate constants for well-defined geometrical rearrangements are intensive quantities, as are the expressions used to calculate them in standard unimolecular rate theory.⁹⁴ In this sense all transitions between the catchment basins of local minima are ‘activated’, since a potential energy barrier is involved, although a more useful definition should probably consider the magnitude of kT or the available energy per degree of freedom.

Our previous results,^{42,43,25,44} now supported by independent calculations,⁹⁵ indicate that the relevant potential energy barriers for diffusion are generally not small compared to kT in the supercooled region. In fact, statistical rate theories have been successfully applied to diffusion

in solids for nearly fifty years, and the standard approach is based on transition state theory for true transition states.⁹⁶ At first sight, these observations might appear to be incompatible with the notion that the system samples mostly higher index saddles above some temperature threshold. However, the analysis of §4 indicates that if the potential energy surface is partitioned into catchment basins of local minima in the usual way then the dynamics can indeed be treated by considering the lowest barriers between them, which are those mediated by true transition states.²⁰ Of course, the usual caveats apply to such an analysis, namely that the transitions are assumed to be Markovian, and a statistical theory is usually employed to calculate the required rate constants, often involving a harmonic approximation.

We have shown how an alternative partitioning scheme based upon Newton-Raphson and eigenvector-following geometry optimisation can successfully divide the potential energy surface into catchment basins associated with all the stationary points. Thermodynamic⁵¹ and dynamic^{62,63,51} schemes might be constructed on this basis along similar lines to the methods used for the conventional partitioning in terms of local minima. However, the latter division is simpler, and the theoretical tools that use it are comparatively well developed.¹²

For weakly interacting subsystems we have now solved the combinatorial problem that defines the number of stationary points of any given index. This analysis also reveals a simple relation between the parameters that determine the total number of stationary points, the number of local minima, and the number of transition states connected on average to each minimum. We have further investigated the displacements corresponding to the Hessian eigenvectors of all the stationary points located using the Newton-Raphson-based scheme of §2 to see whether they are compatible with the above analysis. The results indicate that eigenvectors corresponding to negative eigenvalues involve displacements where fewer atoms participate than for eigenvectors with positive eigenvalues, and that the displacements corresponding to different eigenvectors are more independent. Both these characteristics are most pronounced for stationary points with low values of the Hessian index, in agreement with previous work in which such points are considered as combinations of true transition states for subsystems.⁵¹

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Table 1: Mean total energy, E , potential energy, V , kinetic energy, KE, and kinetic equipartition temperature, T , for seven MD simulations of a BLJ system with number density $1.2\sigma_{AA}^{-3}$.¹² A cutoff of $2.5\sigma_{AA}$ was employed in these calculations together with a shifting scheme that ensured continuity of the energy and gradient.²⁵ The $\pm$ values represent one standard deviation. #min, #ts, #G2 and #NR are the number of distinct minima, transition states, stationary points of $|\nabla V|^2$ and stationary points of V , found for 10^3 searches, using L-BFGS minimisation,^{97, 71} hybrid eigenvector-following transition state searching,⁷² minimisation of $|\nabla V|^2$ using the L-BFGS algorithm, and Newton-Raphson-type steps, respectively (excluding permutational isomers). %SP and %NSP are the percentage of quenches on the $|\nabla V|^2$ surface that converged to stationary points and non-stationary points of V , respectively (out of 10^3 total).²⁵

run	E	V	KE	T	#min	#ts	#G2	#NR	%SP	%NSP
1	-1648.904 ± 0.003	-1723 ± 3	75 ± 3	0.196 ± 0.007	1	188	85	87	17.8	82.2
2	-1599.986 ± 0.005	-1700 ± 4	100 ± 4	0.262 ± 0.005	14	198	419	379	12.6	87.4
3	-1499.959 ± 0.008	-1652 ± 6	152 ± 6	0.399 ± 0.015	592	874	998	995	2.3	97.7
4	-1399.959 ± 0.012	-1602 ± 7	202 ± 7	0.530 ± 0.020	555	892	1000	1000	1.2	98.8
5	-1299.946 ± 0.015	-1536 ± 9	236 ± 9	0.619 ± 0.024	998	1000	1000	1000	1.5	98.5
6	-1199.951 ± 0.020	-1481 ± 11	281 ± 11	0.737 ± 0.028	1000	1000	1000	1000	2.7	97.3
7	-1099.952 ± 0.025	-1427 ± 12	327 ± 12	0.859 ± 0.032	1000	1000	1000	1000	2.3	97.7

Table 2: Mean potential energy differences, ΔV , and displacements, ΔD , between the starting point and the converged geometry after searching for minima (min), transition states (ts), minimising $|\nabla V|^2$ (G2), and performing Newton-Raphson-type (NR) optimisation.¹² The $\pm$ values represent one standard deviation.

run	ΔV_{min}	ΔD_{min}	ΔV_{ts}	ΔD_{ts}	ΔV_{G2}	ΔD_{G2}	ΔV_{NR}	ΔD_{NR}
1	49 ± 2	32 ± 0	44 ± 3	33 ± 1	48 ± 2	32 ± 0	47 ± 5	32 ± 1
2	98 ± 4	33 ± 1	96 ± 5	34 ± 1	96 ± 4	34 ± 1	91 ± 12	34 ± 2
3	147 ± 5	37 ± 1	146 ± 6	37 ± 1	142 ± 6	37 ± 1	121 ± 21	38 ± 2
4	197 ± 8	56 ± 1	195 ± 8	56 ± 1	187 ± 9	56 ± 1	159 ± 22	57 ± 1
5	235 ± 9	133 ± 9	232 ± 9	133 ± 9	205 ± 10	133 ± 9	170 ± 18	133 ± 8
6	283 ± 9	206 ± 11	280 ± 11	206 ± 11	234 ± 12	206 ± 11	192 ± 19	206 ± 11
7	333 ± 13	293 ± 14	329 ± 13	293 ± 14	263 ± 14	293 ± 14	216 ± 21	293 ± 14

Table 3: i_{SP} and i_{NSP} are the fractions of negative Hessian eigenvalues found after minimising $|\nabla V|^2$, split into stationary points and non-stationary points of V , respectively.²⁵ i_{NR} is the corresponding fraction for Newton-Raphson-type searches.¹² The $\pm$ values represent one standard deviation.

run	$i_{\text{NR}} \times 10^3$	$i_{\text{NSP}} \times 10^3$	$i_{\text{SP}} \times 10^3$
1	0.4 ± 0.7	0.4 ± 0.7	0.0 ± 0.0
2	1.4 ± 1.1	1.0 ± 1.0	0.6 ± 0.8
3	4.1 ± 2.1	3.6 ± 1.8	3.2 ± 1.8
4	4.7 ± 2.1	3.5 ± 1.9	3.4 ± 1.5
5	13.6 ± 3.8	10.9 ± 3.2	16.4 ± 3.7
6	21.7 ± 4.3	17.7 ± 3.8	19.5 ± 4.6
7	29.1 ± 4.8	23.9 ± 4.4	25.8 ± 3.4

Figure Captions

1. Mean Hessian index as a function of temperature (canonical ensemble) in reduced units of kT/ϵ for the double well potential $8\epsilon(2x^4 - x^2)$, which has a barrier height of ϵ . The Hessian index calculated for instantaneous configurations and after the Newton-Raphson procedure of §2 give indistinguishable results. The inset shows the same data presented in an Arrhenius plot.
2. Variation of L and $\tilde{N}$, parameters designed to provide insight into the localisation of displacements along Hessian eigenvectors, as a function of the Hessian index. Both parameters were averaged over all the relevant stationary points obtained by Newton-Raphson-type optimisation from configurations sampled in the seven MD runs described in Table 1. For L separate averages were calculated over all pairs of eigenvectors corresponding to negative eigenvalues and all pairs corresponding to positive eigenvalues within each stationary point. For $\tilde{N}$ separate averages were compiled for Hessian eigenvectors corresponding to positive and negative eigenvalues, as indicated.

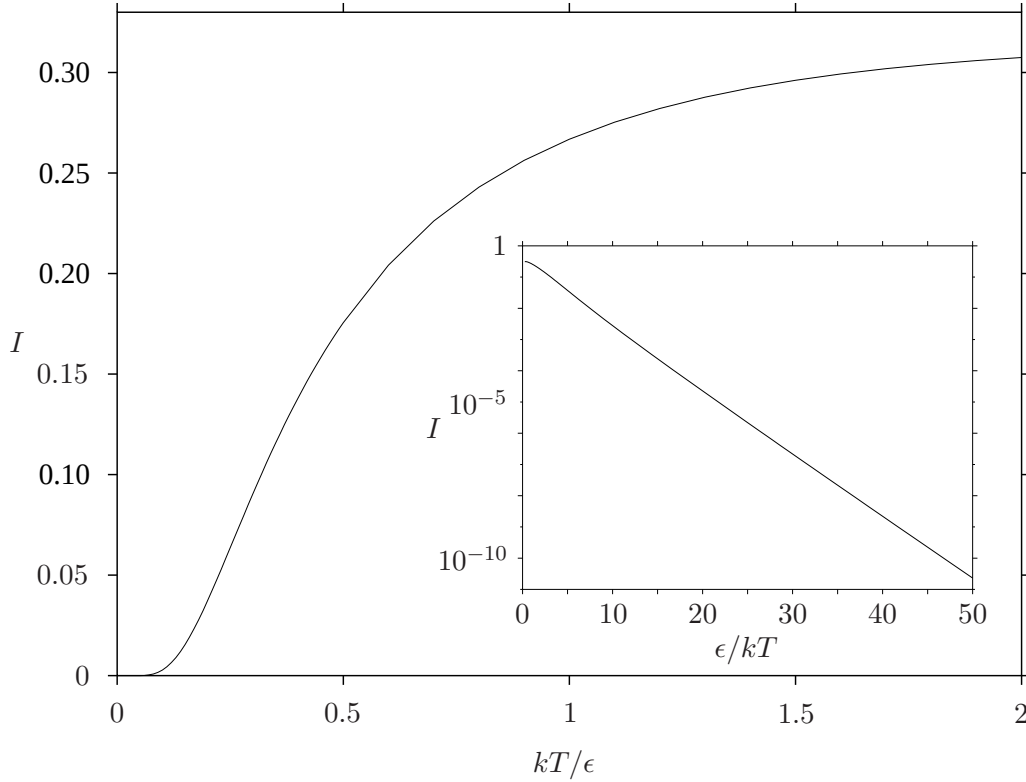


Figure 1:

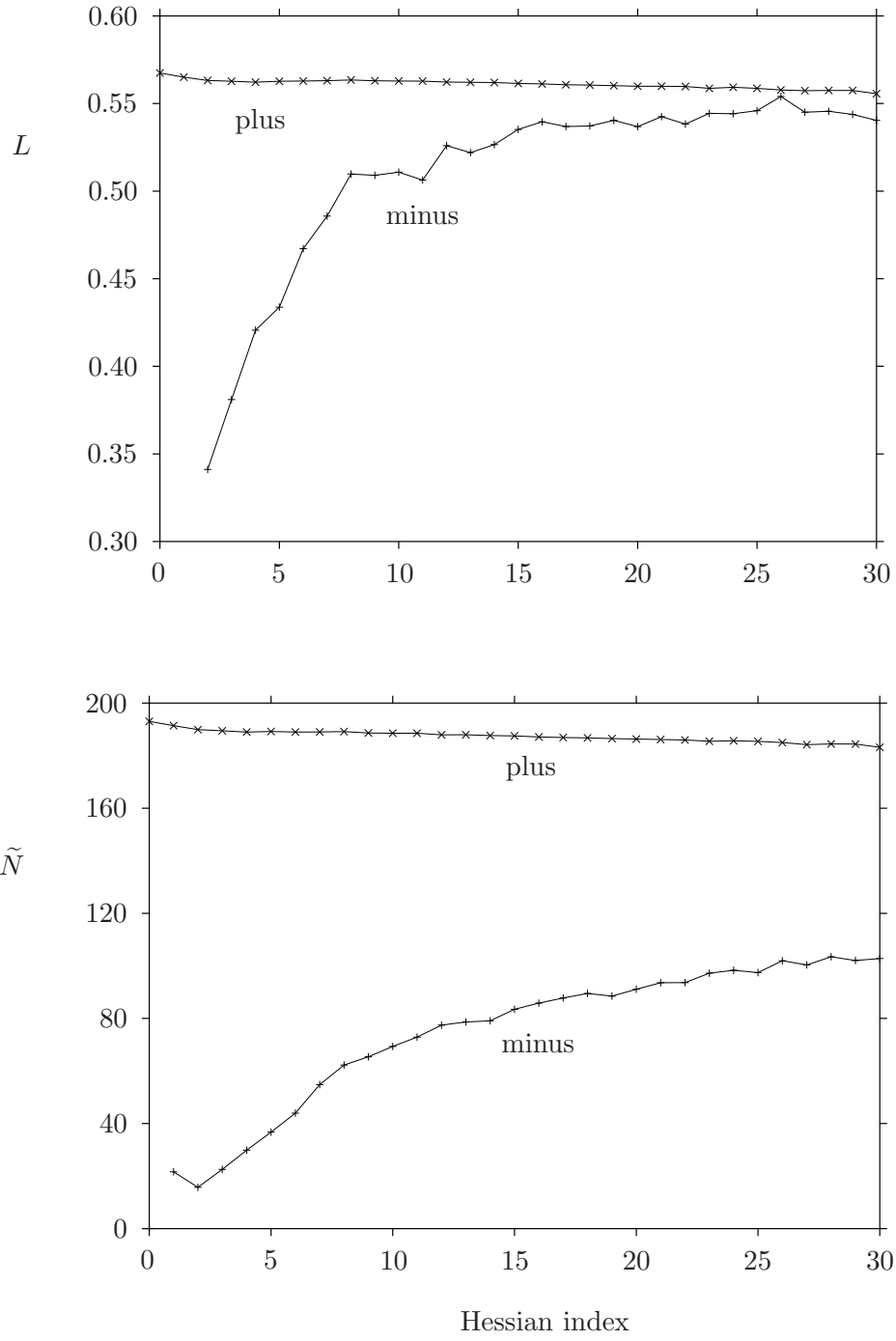


Figure 2: