QUASI-SADDLES OF LIQUIDS: COMPUTATIONAL STUDY OF A BULK LENNARD-JONES SYSTEM

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Abstract

Quasi-saddles or inherent saddles of the potential energy surface, $U$, of a liquid are defined as configurations which correspond to absolute minima of the pseudo-potential surface, $W = |
abla U|^2$, as identified by a multi-dimensional minimisation procedure. The sensitivity of statistical properties of inherent saddles to the convergence criteria of the minimisation procedure is investigated using, as a test system, a simple liquid bound by a quadratically shifted Lennard-Jones pair potential with continuous zeroth, first and second derivatives at the cut-off distance. The variation in statistical properties of saddles is studied over a range of error tolerances spanning five orders of magnitude. The largest value of the tolerance corresponds to that used for the unshifted LJ liquids in a previous work (J. Chem. Phys. 115, 8784 (2001)). Based on our results, it is clear that there are no qualitative changes in statistical properties of saddles over this range of error tolerances and even the quantitative changes are small. The lowest magnitude eigenvalue, $|\omega_0^2|$, of the Hessian is, however, found to be very sensitive to the tolerance; as the tolerance is decreased, $|\omega_0^2|$ is found to show an overall decrease. This indicates that if convergence criteria are not strict, absolute or low-lying minima of $W(r)$ will be diagnosed as having no inflexion directions. The results also show that it is not possible to set up an unambiguous numerical criterion to further classify the quasi-saddles into true saddles which contain no zero curvature, non-translational normal modes and inflexion points which have one or more zero-curvature normal mode directions.
1 Introduction

A number of theoretical approaches have been developed to understand the relationship between the potential energy surface (PES) and the properties of condensed phases. Since the potential energy surface, $U(r)$, is a complicated function of the $3N$ dimensional position coordinates of an $N$-atom system, most approaches have concentrated on identifying features of $U(r)$ most relevant to understanding a particular phenomenon. The most widely used of such energy landscape approaches is inherent structure analysis which focuses on the sampling of local minima of the PES. To perform the inherent structure sampling, configurations are sampled from a well-defined ensemble and are referred to as instantaneous configurations in this work. A steepest-descent or equivalent local minimisation procedure is then initiated for each instantaneous configuration in order to obtain the nearest local minimum. All instantaneous configurations which quench to the same minimum or inherent structure are referred to as belonging to the basin of that minimum. In general, the phase with lowest entropy and internal energy will correspond to location of the system in the basin of the global minima and phase transitions will correspond to occupancy of higher energy metastable minima. Inherent structure analysis has proved to be an extremely useful tool in understanding melting, the glass transition and protein folding. However, it is limited by the fact that it focuses entirely on minima whereas an understanding of dynamical phenomena requires a knowledge of factors which govern the passage of the system between basins of different minima. For example, the dynamical slowing down associated with the glass transition requires an understanding of why rate constants for inter-basin transitions become essentially zero on experimental time scales. In this context, it has recently been suggested that saddle configurations of the PES, which mark the border between adjoining basins of minima, must play a crucial role. Such saddle configurations will have $\nabla U = 0$ and will show negative curvature in one or more orthogonal directions. Saddles of order 1 with just a single negative curvature direction will correspond to a simple transition state connecting two adjacent minima. These stationary points of $U(r)$ will also correspond to absolute minima of the pseudo-potential surface, $W(r) = \frac{1}{2}\nabla U^2$. To identify the saddle points which play a significant role in the system dynamics, it has been suggested that inherent saddles, analogous to inherent structures, can be identified by a steepest descent minimisation from an instantaneous configuration to the nearest local minimum on the pseudo-potential surface, $W(r) = \frac{1}{2}\nabla U^2$, where $U(r)$ is the potential energy as a function of the 3N-dimensional position vector $r$. The statistics of inherent saddles has been recently analysed for several model glass-formers, including a binary Lennard-Jones mixture (BLJ), a modified monoatomic Lennard-Jones (MLJ) liquid and the binary soft-sphere (BSS) mixture. Simulations show that these systems undergo a transition from saddle-dominated to minima-dominated dynamical regimes at the mode-coupling transition temperature, $T_{MC}$. For $T > T_{MC}$, the system is localised largely in border regions and basin-hopping is facile. Below $T_{MC}$, the average saddle order goes to zero implying that the system occupies interiors of the basins of local minima and basin-hopping becomes an activated process. The saddle order is found to be an essentially linear function of the saddle configurational energy. By extrapolating the linear trend one can obtain a threshold energy, $U_{thr}$, at which
the saddle order goes to zero. The average configurational energy at the mode-coupling temperature is found to be very close to $U_{thr}$. Since a glass may be viewed as a very high-viscosity liquid, it is expected that many of the statistical features of the stationary points of the PES of glass-formers will be shared by simple liquids. Recent studies of the stationary points of Lennard-Jones and Morse liquids verify this conjecture [18, 19]. The statistical properties of inherent saddles are shown to carry interesting signatures stemming from variations in generic features of the interatomic potential, such as the range and curvature; for example, the configurational energy is shown to depend linearly on saddle order with a slope that is proportional to the range of the pair potential. These recent studies therefore provide strong evidence that stationary points of the potential energy surface constitute a physically significant set of topographic features of the energy landscape.

The computational strategy for identifying stationary points or inherent saddles in the above studies has been to locate the minima of the pseudo-potential surface, $W(r) = \frac{1}{2} \| \nabla U \|^2$; within the limits of computational precision, the minima for which $W(r) = 0$ are taken to be stationary points [20]. As pointed out in ref. [21], this approach must, however, be applied very carefully because any minimisation algorithm will sample not only absolute minima of $W(r)$ which correspond to the stationary points of the true potential $U(r)$ but also low-lying minima of $W(r)$ which correspond to inflexion points of $U(r)$ [21]. At an inflexion point, the Hessian matrix, $H$, must have one or more zero eigenvalues; the eigenvectors corresponding to these zero eigenvalues do not correspond to basin-crossing displacements. The question therefore arises as to whether the physical significance of inherent saddle analysis is compromised because, given finite numerical precision limits, it may be difficult to distinguish between true saddles and inflexion points. The available numerical studies of this issue are limited but they indicate that the number of inflexion directions is always very small and does not significantly affect the statistical estimates of saddle properties [16, 17]. For example, in the case of the 256 atom MLJ system studied in ref.14, no point with more that four inflexion directions was found. In the liquid regime, the ratio of inflexion directions to negative curvature directions was approximately 0.1. It rises to 0.8 very close to $T_{MC}$ but even then no major shift in the estimated value of $T_{MC}$ was seen.

Given the usefulness of stationary point analysis in understanding liquid-state dynamics, we feel it is worthwhile to perform a detailed computational study of a model system. In this work, we therefore investigate the sensitivity of statistical properties of inherent saddles to details of the minimisation procedure. For this purpose, we define a simple liquid bound by a quadratically shifted Lennard-Jones pair potential with continuous zeroth, first and second derivatives at the cut-off distance. This ensures that no loss of precision in the minimisation procedure is present due to discontinuities in the pair potential at a finite cut-off distance. Previous studies of stationary points of bulk liquids and glasses have used either unshifted pair potentials with long-range corrections [13, 15] or quadratically shifted pair potentials with continuous zeroth and first derivatives but discontinuous second derivatives [12, 13, 14, 15, 16]. The only exception in the literature known to us is the simulation of the binary soft-sphere system but this may represent a special case because of the absence of any attractive tail in the pair potential [17]. Unlike in other studies, we consider a one-component bulk liquid, rather than a binary mixture:
these two classes of systems differ only in the ease with which crystal nucleation
takes place but the crucial statistical features of stationary points are common
to both glass-formers and simple liquids. This monoatomic liquid bound by a
quadratically shifted Lennard-Jones potential (QSLJ) defines a test system for
which we can set reasonably demanding accuracy limits for the minimisation
procedure. The low-lying minima of the pseudo-potential, \( W(r) = \frac{1}{2}|\nabla U|^2 \), as
located by the minimisation procedure are referred to as quasi-saddles; however,
unless the context requires distinguishing clearly between true saddles and in-
flexion points, we also refer to quasi-saddles as saddle configurations. Changes
in various properties of the saddle configurations are analysed as a function of
the precision limits set for the minimisation algorithm. The possibility of setting
up an unambiguous numerical criterion to distinguish between true saddles and
inflexion points is also discussed. This allows us to obtain a useful benchmark
of the degree of error introduced by a given level of convergence in the mini-
minisation procedure. The results should be useful in two contexts. Firstly, it
allows one to estimate the computational effort to be expended in minimisation
given the saddle properties of interest. Secondly, in a number of contexts, it is
of interest to study liquids which do not have a finite range e.g. the Len-
nard-Jones and other well-known model systems. If the statistical analysis of saddle
configurations is to be a generally applicable tool to study the disordered phase
(liquids and glasses), it is essential to establish to what extent such an anal-
ysis will be limited by computational problems associated with the minimisation
procedure. The paper is organised as follows. Section 2 contains details regard-
ing the computational methods employed. Results are presented in Section 3.
Section 4 contains the conclusions.

2 Computational Methods

2.1 Potential Energy Surface

The potential energy surface (PES), \( U(r) \), is defined as a scalar function of the
3N-dimensional position vector, \( r \). The PES studied in this work is pair-additive
i.e.
\[
U(r) = \sum_{i=1}^{N} \sum_{j<i} u_p(r_{ij})
\]  

(1)

where \( r_{ij} \) is the distance between atoms \( i \) and \( j \) and the pair potential, \( u_p(r) \),
is a quadratically shifted Lennard-Jones function of the form
\[
u_p(r) = 4\epsilon \left\{ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right\} + ar^2 + br + c \quad \text{for} \quad r \leq R_c
\]
\[
= 0 \quad \text{for} \quad r > R_c.
\]  

(2)

The \( a, b \) and \( c \) parameters are determined by requiring that \( u_p, du_p/dr \) and
d\(^2u_p/dr^2 \) be zero at \( r = R_c \). We take \( \epsilon, \sigma \) and \( m \) as reduced units for energy,
length and mass respectively; all our results are given in reduced units. The pair
potential defined in equation (2) is referred to as the QSLJ potential in this paper.
The two-parameter quadratically shifted Lennard-Jones potential used
in previous studies of saddles of binary LJ mixtures corresponds to a shifting
function $ar^2 + c$ and is referred to as the SLJ potential. The monoatomic SLJ system was originally discussed in ref.\cite{22}. We fix the spherical cut-off distance at $2.5\sigma$ when computing the shifting parameters. Figure 1 compares the QSLJ, SLJ and unshifted Lennard-Jones (LJ) potentials.

### 2.2 NPT Ensemble Monte Carlo Simulations

All the simulations reported in this paper were performed using the isothermal-isobaric ensemble Monte Carlo method of McDonald \cite{23}. The partition function of an $N$-particle system in this ensemble may be written as:

$$Q_{\text{NPT}} = \frac{\beta P}{\Lambda^{3N} N!} \int d(\ln v) v^{N+1} \exp(-\beta P v) \int ds \exp(-\beta V(s; L))$$  \hspace{1cm} (3)

where $P$ is the external pressure, $\beta = 1/k_B T$ is the inverse temperature, $\Lambda = \sqrt{\hbar^2/2\pi m k_B T}$ is the thermal de Broglie wavelength, $v$ and $L$ are the volume and length of the simulation cell respectively and $s = r/L$ is the 3N-component position vector scaled with respect to the length of the simulation cell. The volume, $v$, and the particle positions, $r$, are the Metropolis variables. The random walk is performed using two types of moves: (i) volume moves which sample in $\ln v$ and (ii) particle moves which displace the spatial coordinates of a single, randomly chosen particle. In the case of the unshifted Lennard-Jones system, long-range corrections were employed and the spherical cut-off distance, $R_c$, was scaled whenever a volume move was made; the average value of $R_c \approx 2.8\sigma$. For the shifted potentials, the cut-off distance was fixed at $2.5\sigma$.

A simulation cell with 125 particles and rhombic dodecahedral boundary conditions was used in the Monte Carlo simulations. The solid phase structure taken to be a face-centred cubic (fcc) lattice. Volume moves constituted 7.4% of trial moves. Acceptance ratios for volume and particle moves were kept at approximately 50%. Run lengths were between two and four million configurations with equilibration periods of one million to two million. This was found to be sufficient to converge configurational averages, such as the average potential energy, density and bond orientational parameters, to better than 1%. In order to obtain statistical averages over inherent saddle configurations, 100 instantaneous configurations were sampled from the NPT-MC simulations at equal intervals and used to generate inherent saddles. The simulations were carried out at a reduced pressure of $P^* = 0.67$. At this pressure, the melting point of the unshifted Lennard-Jones system has been established from previous work as $T^* = 0.75$ \cite{24}.

### 2.3 Locating Inherent Saddles

Locating inherent saddles requires one to find the absolute minima for the pseudo-potential function, $W(r) = \frac{1}{2} |\nabla U|^2$. Any local minimisation technique equivalent to a steepest descent procedure can be used to perform the minimisation. In a previous study \cite{18}, three minimisation procedures for locating inherent saddles were compared: (i) the conjugate gradient algorithm given in ref.\cite{25}, (ii) the variable metric LBFGS algorithm, as implemented by Liu and Nocedal \cite{26} and (iii) Powell's direction set method which requires no gradient information. The LBFGS algorithm was found to be computationally the most
efficient and was therefore used in this study to locate local minima in $W(r)$ using $\nabla W = -H \cdot F$. The termination condition for the LBFGS algorithm is

$$||g_i|| \leq \tau \max(1, ||x_i||)$$ (4)

where $g_i$ and $x_i$ are the gradient and solution vectors for the $i$-th iteration and $|| \cdot ||$ denotes the Euclidean norm. Clearly the more demanding the accuracy requirements i.e. the smaller the error tolerance $\tau$, the more computationally demanding the minimisation procedure will be. This is illustrated in Table 1 which shows the average number of iterations required to converge to the nearest saddle for a given value of $\tau$ for three different temperatures. The error tolerance $\tau$ is the key convergence parameter with respect to which we wish to test the sensitivity of properties of quasi-saddles.

While absolute minima of $W(r)$ must correspond to true stationary points of $U(r)$, local minima in $W(r)$ need not correspond to true stationary points of $U(r)$ with all elements of the gradient vector, $\nabla U$, equal to zero. Some local minima may be inflexion points where both the first and second derivatives in some directions are zero. In principle, such flex points can be distinguished from true saddles by looking at the absolute magnitude of $W(r)$. However, given finite numerical precision it may be difficult to unequivocally distinguish between low-lying and absolute minima. Alternatively, such inflexion points can be located by examining whether any of the eigenvalues of the Hessian for a configuration corresponding to a minimum in $W(r)$, other than the three translational modes, is unusually small. However, the lowest magnitude, non-translational, eigenvalue of the Hessian is very sensitive to the accuracy of the minimisation procedure. Relaxed tolerances can lead to dramatic undercounting of the number of flex points while rigorous convergence criteria lead to almost 99% of local minima of $W(r)$ being identified as inflexion points (for example, one can contrast the results presented in refs. [12] and [16].

3 Results and Discussion

3.1 Isobars of the Quadratically Shifted Lennard-Jones liquid

The behaviour of the quadratically shifted Lennard-Jones system (QSLJ), as defined in Section 2.1, is mapped out along the $P^* = 0.67$ isobar to facilitate comparison with the unshifted Lennard-Jones system. We have also performed NPT ensemble simulations at the same pressure for the two-parameter quadratically shifted Lennard-Jones (SLJ) potential with discontinuous second derivative, as defined by Stoddard and Ford[22]. The binary Lennard-Jones mixtures for which inherent saddle analysis has been performed recently employ the SLJ type of cut-off conditions. Figures 2(a) and 2(b) compare the temperature dependence of the configurational energy per particle and the number density respectively along the $P^* = 0.67$ isobar for the QSLJ, SLJ and LJ systems. The thermodynamic melting temperature, $T^*_m$, is known to be 0.75 for the LJ system at this pressure [24]. The metastability limit of the solid from our NPT simulations is $T^*_k = 0.88$; such a 15-20% difference between $T^*_m$ and $T^*_k$ is fairly typical. Though the difference in the well depth of the pair potential between the LJ and SLJ systems is very small (see Figure 1), the $T^*_k$ values for the SLJ
system is about 13% lower than that of the unshifted LJ system because of the finite-range of the SLJ pair potential. The QSLJ system has an even lower value of $T_k^* = 0.64$ because of the reduced well-depth. At any given temperature, the QSLJ system has the lowest number density and highest configurational potential energy. Since we are interested in the stationary points sampled in the disordered liquid phase, the results of the inherent saddle analysis discussed below refer to liquid state simulations for $T^* \geq 0.75$.

3.2 Sensitivity of Saddle Properties to Accuracy of Minimisation Procedure

A saddle point is characterised by its configurational energy, $U_s$, and its index density, $n_s$, which corresponds to the fraction of imaginary modes; the NPT averages are denoted by $\langle U_s \rangle$ and $\langle n_s \rangle$. In the work of Broderix et al, $\langle U_s \rangle$ and $\langle n_s \rangle$ are referred to as parametric averages with respect to $T$ as the parameter. For the binary LJ mixture, they showed that the points $(\langle U_s \rangle, \langle n_s \rangle)$ lie on a straight line. They also defined the geometric average, $U_s(n_s)$ as the average configurational energy of all saddles of index density $n_s$ and showed that the straight line fits to the geometric and parametric averages are identical, within the limits of statistical error. This linear relationship between the saddle order and configurational energy has been subsequently shown to be true for Lennard-Jones and Morse liquids; moreover, the slope, $\partial U_s / \partial n_s$ has been found to be proportional to the range of the potential [18, 19]. The linear form of the $\langle U_s \rangle(\langle n_s \rangle)$ curves in the disordered, liquid phase can be understood on the basis of a localised mechanism for generating imaginary frequency displacement modes which requires rearrangement of only a few neighbouring atoms.

Figure 3(a) shows the parameteric points $(\langle U_s \rangle, \langle n_s \rangle)$ obtained from minimisations corresponding to three different values of the error tolerance, $\tau = 10^{-10}, 10^{-12}$ and $10^{-15}$. It is well know that error tolerances for systems with finite cut-offs and discontinuous seroth, first or second derivatives cannot be made very small. The tolerance value of $\epsilon = 10^{-10}$ corresponds to that used in a previous study of the unshifted LJ liquid [18]. The tolerances used for the Morse potentials in a more recent study are similar. The slopes of the straight line fits are almost unchanged over five orders of magnitude in $\tau$. The results at $\tau = 10^{-12}$ and $10^{-15}$ are indistinguishable. For $\tau = 10^{-10}$, for a given value of the saddle energy, the saddle order is somewhat overestimated. Figure 3(b) shows the temperature dependence of the ensemble averaged index density. The behaviour with $\tau$ is similar to that seen for the $U_s(n_s)$ curves. Figure 3(c) shows the ensemble-averaged saddle configurational energies as a function of temperature. The convergence with $\tau$ is much better for the saddle energies than for index densities. The reason is that the convergence of the near-zero eigenvalues of the Hessian is relatively strongly affected by the error tolerance compared to the overall saddle configurational energies. To substantiate this point, we have compared the change in the absolute magnitude of the non-translational eigenvalues, $|\omega^2_0|$, of the Hessian with $\tau$ for several configurations. Figure 4 shows the values of the lowest, $|\omega^2_0|$, and third lowest, $|\omega^2_3|$, magnitude eigenvalues of the Hessian for an arbitrary sequence of configurations for $\tau = 10^{-14}$ and $10^{-15}$. The lowest magnitude eigenvalue varies by over a factor of 10 when $\tau$ is reduced by an order of magnitude. There is, on average, a decrease in the magnitude of $\omega^2_0$ as $\tau$ decreases. The magnitudes of the third-lowest eigenvalue (and all other
higher magnitude eigenvalues) are practically unchanged with \( \tau \). The sensitivity of the lowest magnitude eigenvalues of the Hessian to the error tolerance of minimisation is responsible for the relatively large error in \( \langle n \rangle \), compared to \( \langle U \rangle \), discussed above.

3.3 Distinguishing between True Saddles and Inflexion Points

We have approached the possibility of setting up an unambiguous numerical criterion to separate the quasi-saddles into true saddles and inflexion points by comparing the location of each quasi-saddle on a two-dimensional plot with \( x - \) and \( y - \) axes corresponding to \( W(\mathbf{r}_s) \) and \( |\omega_0^2|/\omega_E^2 \) respectively where \( \omega_0^2 \) is the lowest magnitude non-translational eigenvalue of the Hessian (see Figure 5) and \( \omega_E \) is the Einstein frequency. True saddles should correspond to very small values of \( W \) and relatively large values of \( |\omega_0^2| \) and therefore should cluster in the upper left hand corner of the graph. Inflexion points should correspond to relatively larger values of \( W \) and near-zero values of \( |\omega_0^2| \) and therefore should cluster in the lower right hand corner of the graph. If two such well-defined clusters of points are seen, then an unambiguous numerical distinction between true saddles and inflexion points can be made. Figure 5 shows, however, that the situation is quite the opposite. Results for two different temperatures are shown and are representative of the behaviour in other simulation runs. Only a few points (less than 5 in 100) can be classed unambiguously as true saddles; the others form an almost continuous distribution. This is presumably why in ref.16 the use of tight convergence criteria for minimisation led to an identification of 99\% of the quasi-saddles as inflexion points. We suggest that the reason for this behaviour is that in the absence of symmetry constraints requiring some collective normal mode directions of quasi-saddles to have zero curvature, the distinction between saddles and inflexion points is not physically very meaningful because it attempts to distinguish between zero and near-zero curvature situations. Coupled with the fact that the number of near-zero curvature modes is always small, as can be seen even from the saddle normal mode spectra described in ref.18 as well as from the results in ref.19, it would appear that the effect of reducing \( \tau \) will be to introduce small corrections in the saddle index density. Since the physical significance of such quasi-saddles stems from the fact that the majority of negative curvature directions will correspond to basin-crossing displacements, improving the error tolerance will not qualitatively alter any results.

4 Conclusions

The purpose of this study was to test the sensitivity of statistical properties of quasi-saddles of the potential energy surface, \( U(\mathbf{r}) \), to the convergence criteria used for minimisation on the pseudo-potential surface, \( W(\mathbf{r}) = |\nabla U|^2 \).

For this purpose a quadratically shifted Lennard-Jones (QSLJ) pair potential was defined which has continuous zeroth, first and second derivatives at the cut-off distance. Inherent saddles (or quasi-saddles) of the bulk QSLJ liquid were studied as a function of the error tolerance, \( \tau \), of the LBFGS minimisation algorithm. The variation in statistical properties of saddles was studied over a range of \( \tau \) values covering five orders of magnitude. The largest \( \tau \) values
correspond to those used for unshifted LJ and Morse liquids simulations previously. Based on our results, it is clear that there are no qualitative changes in statistical properties of saddles over this range of error tolerance and even the quantitative changes are small. The ensemble-averaged saddle index densities were found to be more sensitive to $\tau$ than the corresponding averages over saddle configurational energies. The lowest magnitude eigenvalue, $|\omega_0|^2$, of the Hessian was, however, found to be very sensitive to the tolerance; as $\tau$ was decreased, $|\omega_0|^2$ was found to show an overall decrease. This indicates that if convergence criteria are not strict, absolute or low-lying minima of $W(r)$ will be diagnosed as having no inflexion directions, as was found in ref. 12 and 18. For the smallest value of $\tau$, we also considered the possibility of setting up a numerical criterion to clearly distinguish between true saddles and inflexion points by considering the value of both $W(r)$ as well as $|\omega_0|^2$ at a quasi-saddle identified by minimisation on the pseudo-potential surface. We find however, that the quasi-saddles do not fall into two such clear and distinct categories. The reason appears to be that of the $3N$ normal mode directions associated with a low-lying or absolute minima of $W(r)$, a few directions will correspond to near-zero curvatures. Deducing which of these near-zero curvatures is actually identically equal to zero and therefore corresponds to an inflexion direction is necessary in order to distinguish between true saddles and inflexion points. Moreover, this appears not to be a physically very meaningful distinction since the physically important feature of quasi-saddles is the existence of negative curvature directions indicating their location at the border between adjacent minima.

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References

[1] F. H. Stillinger and T. A. Weber, Phys. Rev. A 25, 978 (1982); Science 225, 983 (1984).

[2] F. H. Stillinger, Science 267, 1935 (1995).

[3] J. P. K. Doye and D. J. Wales Science 271, 484 (1996).

[4] D. J. Wales, J. P. K. Doye, M. A. Miller, P. N. Mortenson and T. R. Walsh, Adv. Chem. Phys. 115, 1 (2000).

[5] C. A. Angell, Science 267, 1924 (1995).

[6] L. Angelani, G. Parisi, G. Ruocco and G. Viliiani, Phys. Rev. Lett. 81, 4648 (1998).

[7] S. Sastry, Nature 409, 164 (2001).

[8] L. -M. Matinez and C. A. Angell, Nature 410, 663 (2001).

[9] A. Scala, F. W. Starr, E. L. Nave, F. Sciortino and H. E. Stanley, Nature 496, 166 (2000).

[10] O. M. Becker and M. Karplus, J. Chem. Phys. 106, 1495 (1997).

[11] J. N. Onuchic, Z. Luthey-Schulten and P. G. Wolynes, Ann. Rev. Phys. Chem. 48, 545 (1997).

[12] L. Angelani, R. Di Leonardo, G. Ruocco, A. Scala and F. Sciortino, Phys. Rev. Lett. 85, 5356 (2000).

[13] K. Broderix, K. K. Bhattacharyya, A. Cavagna, A. Zippelius and I. Giardina, Phys. Rev. Lett. 85, 5360 (2000).

[14] L. Angelani, R. Di Leonardo, G. Parisi and G. Ruocco, Phys. Rev. Lett. 87, 055502-1 (2001).

[15] A. Scala, L. Angelani, R. Di Leonardo, G. Ruocco and F. Sciortino (cond-mat/0106065).

[16] L. Angelani, R. Di Leonardo, G. Ruocco, A. Scala and F. Sciortino, J. Chem. Phys. (to be published).

[17] T. S. Grigera, A. Cavagna, I. Giardina and G. Parisi, Phys. Rev. Lett. 88, 055502 (2002).

[18] P. Shah and C. Chakravarty, J. Chem. Phys. 115, 8784 (2001).

[19] P. Shah and C. Chakravarty (submitted for publication).

[20] F. H. Stillinger and T. A. Weber, J. Chem. Phys. 81, 5095 (1984).

[21] J. P. K. Doye and D. J. Wales, J. Chem. Phys. 116, 3777 (2002).

[22] S. D. Stoddard and J. Ford, Phys. Rev. A 8, 1504 (1973).
[23] D. Frenkel and B. Smit, *Understanding Molecular Simulation: From Algorithms to Applications* (Academic Press, Boston, 1996).

[24] J.-P. Hansen and L. Verlet, *Phys. Rev.* **184**, 151 (1969).

[25] W. H. Press, B. P. Flannery, S. A. Teukolsky and W. T. Vetterling, *Numerical Recipes in Fortran* (Cambridge University Press, Cambridge, 1990)

[26] D. C. Liu and J. Nocedal, *Mathematical Programming* **45**, 503 (1989)
Table 1
Average Number of iterations of the LBFGS minimisation algorithm for a given error tolerance, $\tau$, at a reduced temperature $T^*$ for the quadratically shifted Lennard-Jones (QSLJ) liquid.

| $T^*$  | $\tau = 10^{-10}$ | $\tau = 10^{-12}$ | $\tau = 10^{-14}$ |
|-------|-------------------|-------------------|-------------------|
| 0.67  | 66                | 1306              | 11469             |
| 0.88  | 54                | 1077              | 10895             |
| 1.29  | 35                | 898               | 17362             |
Figure Captions

1. Comparison of the quadratically shifted Lennard-Jones (QSLJ) pair potential with continuous zeroth, first and second derivatives with the two-parameter quadratically shifted Lennard-Jones (SLJ) potential defined in ref.22 as well as the unshifted Lennard-Jones (LJ) potential. The well-depth, \( \epsilon \), and size parameter, \( \sigma \), of the LJ potential are taken as reduced units of energy and length respectively.

2. Dependence of configurational properties on reduced temperature \( T^* \) at a reduced pressure \( P^* = 0.67 \) for the bulk LJ, SLJ and QSLJ systems: (a) average potential energy per particle \( \langle U^* \rangle \) and (b) reduced density \( \rho^* \).

3. Statistical properties of saddle configurations for three different values of the error tolerance, \( \tau \), used in the LBFGS minimisation algorithm: (a) Parametric averages of saddle configurational energies, \( \langle U \rangle_s \), versus index densities, \( \langle n \rangle_s \) (b) saddle index densities as a function of the reduced temperature, \( T^* \) and (c) saddle configurational energies, \( \langle U \rangle_s \), as a function of the reduced temperature, \( T^* \). Configurational energies \( U \) are in units of \( \epsilon \) per particle.

4. Sensitivity of the lowest magnitude, \( |\omega_0^2| \), and third lowest magnitude, \( |\omega_2^2| \) eigenvalues of the Hessian for a set of 20 saddle configurations sampled from the simulation at \( T^* = 1.05 \) for \( \tau = 10^{-14} \) and \( 10^{-15} \). The y-axis has a logarithmic scale.

5. Scatter plots showing the correlation of the \( |\omega_0^2|/\omega_E^2 \) values with the value of the pseudo-potential, \( W(r) = |\nabla U|^2 \), for saddle configurations sampled from simulations at two different temperatures where \( \omega_E \) is the Einstein frequency.
Figure 1

The diagram shows the potential energy $u_p(r)$ as a function of the reduced distance $r/\sigma$ for different systems. The curves represent different models:

- **LJ** (solid line)
- **SLJ** (dashed line)
- **QSLJ** (dotted line)

The inset highlights the behavior at small $r/\sigma$ values.
Figure 2(a)

Graph showing the relationship between $T^*$ and $\langle U^* \rangle$ for different models: QSLJ, SLJ, and LJ.
Figure 2(b)
Figure 3(a)
Figure 3(c)

\begin{align*}
\tau = 10^{-10} & \quad \square \quad \text{---} \\
\tau = 10^{-12} & \quad \circ \quad \text{---} \\
\tau = 10^{-15} & \quad \nabla \quad \text{---}
\end{align*}
Figure 4

Lowest: $\tau=10^{-15}$
$\tau=10^{-14}$

$|\omega_i|^2$ vs Configuration Number
Figure 5

\[ \frac{|\omega_0^2|}{\omega_E^2} \]

\[ W(r_s) \]

\( T^* = 0.75 \)

\( T^* = 1.287 \)