Saddles on the potential energy landscape of a Lennard-Jones liquid 1

Kurt Broderix*, Kamal K. Bhattacharya*, Andrea Cavagna†, Annette Zippelius* and Irene Giardina**

* Institut für Theoretische Physik, Universität Göttingen, D-37073 Göttingen, Germany
† Department of Physics and Astronomy, The University, Manchester, M13 9PL, UK
** Service de Physique Théorique, CEA Saclay, 91191 Gif-sur-Yvette, France

Abstract. By means of molecular dynamics simulations, we study the stationary points of the potential energy in a Lennard-Jones liquid, giving a purely geometric characterization of the energy landscape of the system. We find a linear relation between the degree of instability of the stationary points and their potential energy, and we locate the energy where the instability vanishes. This threshold energy marks the border between saddle-dominated and minima-dominated regions of the energy landscape. The temperature where the potential energy of the Stillinger-Weber minima becomes equal to the threshold energy turns out to be very close to the mode-coupling transition temperature $T_c$.

The low temperature dynamics of supercooled liquids and glasses is often put in relation with the geometric properties of the potential energy landscape of these systems. In particular, the presence of a large number of inequivalent glassy minima has stimulated many studies in the past [1–5]. More recently, the study of mean-field models of spin-glasses has strengthened the persuasion that the dynamical behaviour of glassy systems is deeply connected to the topology of the energy landscape [6]. Moreover, it has been shown that spin-glass systems exhibiting one-step replica symmetry breaking (1RSB) have many dynamical properties in common with fragile structural glasses [7], suggesting that 1RSB mean-field spin-glasses and fragile glasses may have a similar energy landscape.

In this context, crucial questions are: How to characterize the energy landscape of a glassy system? How to quantify the similarity of the energy landscape of fragile glasses and 1RSB spin-glasses? Although utterly relevant, the structure of minima of the potential energy is not enough: even at low temperatures, when activation is the only mechanism of diffusion in liquids, overcoming a barrier implies crossing a saddle of the potential energy. Furthermore, at higher temperatures the system spends more time around saddles than minima, hence the structure of unstable stationary points is important for understanding the crossover from a non-activated to an activated dynamics upon cooling [8,9]. The statistical properties

---

1) Invited talk presented at the Conference Disordered and Complex Systems, King’s College London, July 2000.
of the stationary points of the potential energy are of course independent of the
temperature, as also should be a thorough description of the energy landscape itself.

Here we will focus on the purely geometric properties of the energy landscape of a
glassy system, by studying the statistical properties of all the stationary points of its
potential energy, be they minima or saddles. We classify them according to number
of unstable directions, (or index K), potential energy and smallest eigenvalue of the
Hessian matrix. We show that in this way it is possible to quantitatively compare
the energy landscape of different systems, pointing out similarities and differences.
Moreover, we discover a threshold energy below which it is highly unlikely to find
saddles and the relaxation requires activation. We thus establish a connection
between this threshold energy and the critical temperature \( T_c \) of mode-coupling
theory (MCT) [10]. Finally, by means of our results, we support some recent
speculations on the role of saddles in supercooled liquids [9].

The system under consideration is a binary mixture of Lennard–Jones (LJ) parti-
cles [11] (for details see [12]). Throughout this study we present results for systems
with \( N = 60 \) particles. In order to explore the stationary points of the potential
energy, we use the following method: We equilibrate a configuration at a given
temperature \( T \) using a standard molecular dynamics (MD) simulation technique.
To locate a saddle close to the equilibrium configuration we then perform a quench
on a pseudo-potential energy landscape \( W(x) \) given by the modulus square of the
force, \( W(x) = \nabla^2 U(x) \cdot \nabla U(x) \), where \( U(x) \) is the original potential energy [12,13].
All absolute minima of \( W(x) \) are stationary points of \( U(x) \), hence every saddle of
\( U(x) \) has a well defined basin of attraction. The local minima of \( W(x) \), however, do
not correspond to zeros of the real force. These points are frequently sampled, but
they can easily be distinguished from the absolute minima and are excluded from
our analysis. However, this means that the method does not associate to all the
configurations a nearby saddle and therefore it cannot be used to build a natural
dynamics of the relevant saddles, equivalent to the Stillinger-Weber (SW) one for
minima [2]. Furthermore, the relation between the initial MD equilibrium configu-
ration at temperature \( T \) and the final stationary point found by this algorithm, is
not straightforward. We prefer to perform here a purely geometric analysis of the
stationary points, independent of the way we have sampled them [14].

Given a stationary point, we compute its index density \( k = K/(3N) \) and its
potential energy density \( u = U/N \). In Fig.1 we show the results obtained by
sampling saddles at two different values of the temperature. This plot clearly
suggests that there is an underlying curve \( k(u) \) independent of the temperature,
which encodes a purely geometric feature of the landscape. By sampling stationary
points at different values of \( T \) we are simply exploring different portions of the same
geometric curve: temperature acts as a light spot needed to unveil the underlying
function \( k(u) \). In Fig.2 we show the average index density as a function of the
energy density. What is most striking of this plot is how well defined the function
\( k(u) \) is: due to its geometric nature there are no thermal fluctuations. This curve
shows that if we cut the potential energy landscape with a plane of constant energy
density $u = u_0$, the stationary points on this plane (or within a narrow shell around this plane) will be dominated by saddles with index density $k(u_0)$. Furthermore, $k(u)$ is to a very good approximation a linear function in the explored regime of $u$. This implies that the curve extrapolates to zero at a well defined energy, which we call the threshold energy $u_{th}$, in analogy with 1RSB spin-glasses. The linear interpolation of all the data and the linear interpolation of the last four points give the same estimate for the threshold, that is $u_{th} = -4.55$.

The threshold energy marks the border between the saddles-dominated portion of the energy landscape and the minima-dominated one. A crucial point is that $u_{th}$ is above the energy of the deepest glassy minima found with the SW method [2], that is $u_0 = -4.65$: there is a finite energy density interval, $u \in [u_0, u_{th}]$, where minima are entropically dominant over saddles, as it happens in 1RSB spin-glasses [15]. In those systems, however, $k(u)$ is not a linear function and $k'(u)$ vanishes at the threshold. This difference may be related to the mean-field nature of 1RSB models as opposed to real liquids. Indeed, in [9] the slope of $k(u)$ has been connected to the energy barriers in the system by the relation $\Delta U \sim 1/k'(u)$: in the mean-field case we expect barriers among minima to diverge, implying $k'(u_{th}) = 0$ (as found in 1RSB models), while this cannot be true in finite dimensional systems.

To further compare the energy landscape of LJ and 1RSB systems, we consider in Fig.3 the lowest eigenvalue $\lambda_0$ of the Hessian in a stationary point, as a function of its potential energy density. As expected, $\lambda_0 \to 0$ for $u \to u_{th}$, implying that the potential energy landscape at the threshold has some flat directions, i.e. it is marginal [6]. What is somewhat surprising is that $\lambda_0(u)$ is approximately a
linear function of the energy, $\lambda_0 \sim (u_{th} - u)$, exactly as in 1RSB spin-glasses [17]. We conclude that both, the index density $k(u)$ and the smallest eigenvalue $\lambda_0(u)$, provide a quantitative measure and allow a direct comparison of the properties of the energy landscape for two very different systems, LJ liquids and 1RSB mean-field spin-glasses.

Our next task is to relate the threshold potential energy $u_{th}$ to the dynamical behaviour of the supercooled liquid in the proximity of the glass transition. In Fig.4 we plot the average energy density $u_{SW}(T)$ of the SW minima as a function of the temperature of the initial MD trajectory [3–5], in comparison to $\delta(T) \equiv \langle U(x)/N \rangle(T) - 3/2T$, i.e. the difference between the average potential energy density (from MD simulations) and the vibrational energy in the harmonic approximation. For a harmonic potential $\delta(T)$ is just the energy of the minimum of the well. We find that $\delta(T) \sim u_{SW}(T)$ for $T \leq 1.2$ [16]. This is the range of temperatures which is dominated by the energy landscape and the timescales for the two processes of relaxation - vibrations inside a minimum and hopping between different minima - start to separate. Close to the glass transition (depending on the cooling rate) the system falls out of equilibrium, as indicated by the saturation of both quantities, $u_{SW}(T)$ and $\delta(T)$. As we can see, the extrapolation of the equilibrium part of these curves reaches the threshold energy at the MCT transition temperature $T_c$. The index density vanishes at the threshold, so that below this energy minima are the entropically dominant stationary points. Of course, there are minima also above the threshold, but they are not dominant, while saddles are. The MCT $T_c$ therefore corresponds to the temperature below which minima visited

**FIGURE 2.** Index density as a function of the potential energy density. Average over all the data obtained by sampling at $T \in [0.3, 2.0]$. The full line is a linear fit of the data.
by the dynamics become entropically dominant, while saddles become statistically irrelevant.

To conclude, we consider the potential energy barriers between different minima in our system. According to [9] we can obtain an estimate of the barriers from the slope of $k(u)$, as $\Delta U = 1/[3k'(u_{th})] \sim 5.0$, which has the right order of magnitude (see, for example, the data of [18]). Following the scenario of [9], we must locate the geometric crossover temperature $T_B$, below which saddles no longer contribute to diffusion: as we have seen above, this temperature must be identified in this system with $T_c$, giving $T_B \sim 0.44$. On the other hand, the other crossover temperature $T_A$, ruling activation, is fixed by the barrier size, $T_A \sim \Delta U \sim 5.0$. Hence, for this system we have $T_B < T_A$: at $T_B$ barriers are already quite large as compared to $T$, and following [9] this implies that the system is fragile. This result is consistent with the common classification of LJ liquids as fragile and therefore supports the description of fragile vs strong liquids behaviour given in [9].

REFERENCES

1. M. Goldstein, J. Chem. Phys 51, 3728 (1969).
2. F.H. Stillinger and T.A. Weber, Phys. Rev. A 25, 978 (1982).
3. H. Jonsson and H.C. Andersen, Phys. Rev. Lett. 60, 2295 (1988);
4. S. Sastry, P.G. Debenedetti and F. Stillinger, Nature, 393, 554 (1998).
5. K. K. Bhattacharya, K. Broderix, R. Kree and A. Zippelius, Europhys. Lett. 47, 449 (1999)
FIGURE 4. Triangles represent the energy of the Stillinger-Weber minima $u_{sw}$ as a function of the temperature of the initial MD trajectory. Circles represent the quantity $\delta(T)$. The MCT transition is at $T_c \sim 0.44$.

6. See, for example, J.-P. Bouchaud, L.F. Cugliandolo, J. Kurchan and M. Mézard, in Spin Glasses and Random Fields, Singapore: Worlds Scientific Publishing, 1998, editor A.P. Young; pp. 161-223, and references therein.

7. W. Kob and J.-L. Barrat, Phys. Rev. Lett. 78, 4581 (1997).

8. B. Madan and T. Keyes, J. Chem. Phys. 98, 3342 (1992).

9. A. Cavagna, preprint cond-mat/9910244 (1999).

10. U. Bengtzelius, W. Goetze and A. Sjolander, J. Phys. Chem. 17, 5915 (1984); E. Leutheusser, Phys. Rev. A 29, 2765 (1984).

11. W. Kob and H. C. Andersen, Phys. Rev. Lett. 73, 1376 (1994); Phys. Rev. E 51, 4626 (1995).

12. K. Broderix, K.K. Bhattacharya, A. Cavagna, A. Zippelius and I. Giardina, preprint cond-mat/0007258 (2000).

13. L. Angelani, R. Di Leonardo, G. Ruocco, A. Scala and F. Sciortino, preprint cond-mat/0007241 (2000).

14. A quench on the pseudo-potential $W(x)$ is likely to decrease on average the real energy $U(x)$ as a consequence of the fact that the Hessian has more positive than negative eigenvalues. The increment of the energy during a gradient descent step, $\delta x = -\nabla W dt$, is given by: $dU = \nabla U \cdot \delta x = -\nabla U \cdot \nabla W dt = -\nabla U \cdot \mathcal{H} \cdot \nabla U dt$, where $\mathcal{H}$ is the Hessian of $U$, which at low energies has only a small fraction of negative eigenvalues. Thus, if $\mathcal{H}$ and $\nabla U$ are weakly correlated, we do expect the quadratic form $\nabla U \cdot \mathcal{H} \cdot \nabla U$ to be positive on average, and therefore $dU$ to be negative.

15. A. Cavagna, I. Giardina and G. Parisi, Phys. Rev. B 57, 11251 (1998).

16. See also S. Sastry, J. Phys.: Condens. Matter 12, 6515 (2000).
17. J. Kurchan, G. Parisi and M.A. Virasoro, *J. Phys. I France* **3**, 1819 (1993);
18. T.B. Schröder, S. Sastry, J.C. Dyre and S. Glotzer, *J. Chem. Phys.* **112**, 9834 (2000).