Saddles and softness in simple model liquids

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NOTES

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The analysis of the potential energy landscape (PEL) of model liquids has allowed to clarify many interesting phenomena of the supercooled liquid regime and the slowing down of the dynamics. More recently a promising PEL description was obtained studying the properties of saddle points.9–12 In a previous work,13 some of us reported a new analysis was obtained studying the properties of saddle minima versus T, energy elevation of saddles of order 1 from underlying minima versus n, when temperatures and energies are scaled by mode-coupling temperature T_MCT (we set k_B=1); (ii) a nearly constant ratio between elementary saddle energy barriers and energy elevation of saddles of order 1 from underlying minima and T_MCT: 

\[ \Delta E = 10 T_MCT \]

(iii) a quantitative relationship between \( \Delta E \) and the Arrhenius activation energy \( \Delta E_{\text{Arr}} \) (obtained from low-T diffusivity), \( \Delta E_{\text{Arr}} = 2 \Delta E \). Although obtained for different models, the reported universality was not too surprising due to the similar shape of the repulsive part of the pair potential, in particular all having the same \( r^{-12} \) dependence. For this reason a wider class of models must be analyzed in order to show the robustness of the reported universality.

In this note we extend the class of model liquids under consideration, analyzing soft spheres with different power n of the interparticle repulsive potential (different softness).14 We find that systems interacting with \( r^{-n} \) potential belong to the same universality class of LJ-like potentials, thus pointing towards a common organization of saddles in the PEL of disordered systems.

The investigated systems are 80:20 binary mixtures of N=1000 particles enclosed in a cubic box with periodic boundary conditions and interacting through the pair potential

\[ V_{\alpha\beta}(r) = 4\varepsilon_{\alpha\beta} \left( \frac{\sigma_{\alpha\beta}}{r} \right)^n, \]  

where \( \alpha, \beta \in \{A, B\} \), \( \sigma_{AA} = 1.0, \sigma_{AB} = 0.8, \sigma_{BB} = 0.88 \), \( \varepsilon_{AA} = 1.0, \varepsilon_{AB} = 1.5, \varepsilon_{BB} = 0.5 \). Reduced units will be used in the following [\( \sigma_{AA} \) for length, \( \varepsilon_{AA} \) for energy, \( \left(m\sigma_{AA}^2/\varepsilon_{AA}\right)^{1/2} \) for time—m is the mass of the particles]. The analyzed density was \( \rho = 1.2 \). The investigated values of the parameter n tuning the softness of the interaction were \( n = 6, 8, 12, 18 \). We note that for \( n < 6 \) crystallization events prevent the study of the supercooled regime. Following previous works,9 we studied the properties of the saddles of the PEL visited by the system during its dynamic evolution at a given temperature (performed through isothermal molecular dynamics simulations with Nosé-Hoover thermostat). The temperature range investigated is such that, for each n, the diffusivity covers about four orders of magnitude. Saddles are located using minimization procedures (LBFGS algorithm as implemented by Liu and Nocedal15) on the pseudo-potential \( W = |V|^2 \) (V is the total potential energy). Inher-

FIG. 1. Saddle order \( n_s \) as a function of \( T/T_{\text{MCT}} \) for the model systems of this work (soft spheres with different softness n) together with the data obtained in a previous work for LJ-like models (Ref. 13). Dashed line is a power-law fit, while full line is a REM-like fit (Ref. 19).
The energy elevation, now scaled by $T_{\text{MCT}}$, is plotted versus $n_s$. The data collapse onto a master curve, with a mean slope $m = m'/T_{\text{MCT}} = 30$, indicating that the different soft sphere models have a similar landscape organization with the same elementary energy barrier height when expressed in unit of $T_{\text{MCT}}$: $\Delta E/T_{\text{MCT}} \approx 10$. We note, however, a small correlation between the slope and the value of $n$, with lower values of $n$ associated to higher values of the slope. Also reported in Fig. 2 are the data obtained in the previous work, suggesting a wider universality of the relationship $\Delta E \approx 10 T_{\text{MCT}}$.

A last observation arises from the analysis of Arrhenius energy barriers $\Delta E_{\text{Arr}}$, obtained from Arrhenius fits $\exp(-\Delta E_{\text{Arr}}/T)$ of the low-$T$ diffusivity data (see Ref. 13). Expressed in unit of $T_{\text{MCT}}$ one obtains, for different softness $n$, values of $\Delta E_{\text{Arr}}$ in the range 21–24. Again this finding is in agreement with the previous observation for LJ-like models: $\Delta E_{\text{Arr}} \approx 2 \Delta E$.

In conclusion, the analysis of soft sphere models with different softness confirms the results previously obtained for LJ-like models, supporting the hypothesis of a universal relation controlling the structure of the PEL.