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LETTERS TO THE EDITOR

The Letters to the Editor section is divided into three categories entitled Notes, Comments, and Errata. Letters to the Editor are limited to one and three-fourths journal pages as described in the Announcement in the 1 July 2004 issue.

NOTES

Saddles and softness in simple model liquids

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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.[1–8] 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 numerical investigation of the PEL for different Lennard-Jones (LJ)-like model liquids, focusing on the properties of saddle points visited by the systems at different temperatures. The main findings of that work were (i) the existence of master curves for saddle-based quantities (saddle order n_s versus T, energy elevation of saddles from underlying minima versus n_s) 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 ΔE (energy elevation of saddles of order 1 from underlying minima) and T_{MCT}, $\Delta E \simeq 10 T_{\mathrm{MCT}}$; (iii) a quantitative relationship between ΔE and the Arrhenius activation energy ΔE_{Arr} (obtained from low-T diffusivity), $\Delta E_{\mathrm{Arr}} \simeq 2\Delta E$. 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

$$V_{\alpha\beta}(r)=4\epsilon_{\alpha\beta}\left(\frac{\sigma_{\alpha\beta}}{r}\right)^{n}, \tag{1}$$

where $\alpha,\ \beta \in A,\ B,\ \sigma_{AA}=1.0,\ \sigma_{AB}=0.8,\ \sigma_{BB}=0.88,\ \epsilon_{AA}=1.0,\ \epsilon_{AB}=1.5,\ \epsilon_{BB}=0.5$.[15,16] Reduced units will be used in the following [σ_{AA} for length, ϵ_{AA} for energy, $(m\sigma_{AA}^2/\epsilon_{AA})^{1/2}$ 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 Nocedal[17]) on the pseudopotential $W=|\nabla V|^2$ (V is the total potential energy). Inher-

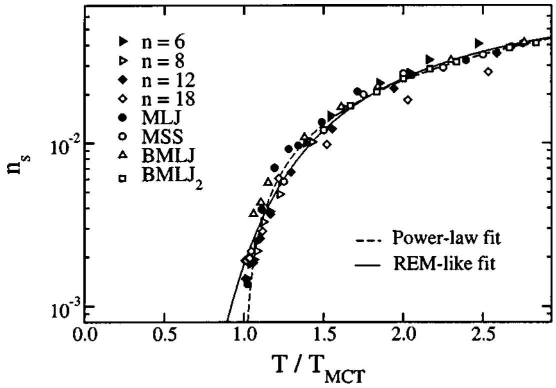

FIG. 1. Saddle order n_s as a function of T/T_{MCT} for the model systems of this work (soft spheres with different softness n) together with the data obtained in a previous work for LJ-like models (Ref. 13). Dashed line is a power-law fit, while full line is a REM-like fit (Ref. 19).

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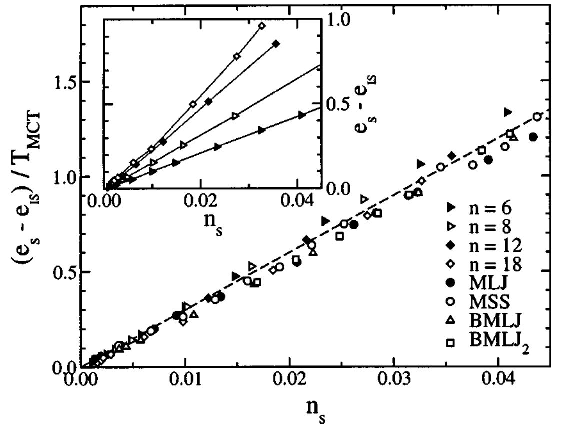

FIG. 2. Energy elevation (rescaled by T_{MCT}) of saddles from underlying minima $(e_s - e_{IS})/T_{\mathrm{MCT}}$ against saddle order n_s, for the systems of this work (soft spheres with different softness n) and for LJ-like models (Ref. 15). The straight line has slope 30, corresponding to an elementary energy barrier $\Delta E/T_{\mathrm{MCT}} = 10$. In the inset the same quantity not rescaled by T_{MCT} for the soft sphere models.

ent structures are also located (minimizing the true potential V) at each temperature. We then collected the properties of saddles (energy e_s and order n_s defined as the number of negative eigenvalues of the Hessian of V) and inherent structures (energy e_{IS}).

In Fig. 1 we show the saddle order n_s as a function of T/T_{MCT} (T_{MCT} is the mode-coupling temperature estimated from the power-law divergence of inverse diffusivity) for different values of softness n. In the figure we report also the same quantity for the LJ-like systems analyzed in a previous work.[13] All the data collapse onto a master curve, even if some deviation is present, in particular for $n = 6$ and $n = 18$. In a first approximation scaling T by T_{MCT} gives rise to a common behavior of the analyzed quantity for the different models. It is worth noting that a similar master plot has been obtained in Ref. 18 for LJ and CS_2 systems.

Looking at the mean energy elevation $e_s - e_{IS}$ of saddles from underlying minima as a function of saddle order n_s (inset in Fig. 2), one obtains nearly straight lines, with different slopes for different values of n. This indicates a simple organization of the PEL, with saddles equispaced in energy above underlying minima, and allows to define an elementary energy barrier elevation ΔE from the slopes m' of the curves: $\Delta E = m'/3$ (the factor 3 arises from the definition of n_s as the number of negative eigenvalues of the Hessian normalized to the number of degrees of freedom $3N$). From the inset in the figure one observes that different softness give rise to different ΔE values. In the main panel of Fig. 2 the energy elevation, now scaled by T_{MCT}, is plotted versus n_s. The data collapse onto a master curve, with a mean slope $m = m'/T_{\mathrm{MCT}} = 30$, 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_{MCT}: $\Delta E/T_{\mathrm{MCT}} \simeq 10$. 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,[13] suggesting a wider universality of the relationship $\Delta E \simeq 10 T_{\mathrm{MCT}}$.

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

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.

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