

## Saddles in the Energy Landscape: Extensivity and Thermodynamic Formalism

M. Scott Shell, Pablo G. Debenedetti, and Athanassios Z. Panagiotopoulos

*Department of Chemical Engineering, Princeton University, Princeton, New Jersey 08544, USA*

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We formally extend the energy landscape approach for the thermodynamics of liquids to account for saddle points. By considering the extensive nature of macroscopic potential energies, we derive the scaling behavior of saddles with system size, as well as several approximations for the properties of low-order saddles (i.e., those with only a few unstable directions). We then cast the canonical partition function in a saddle-explicit form and develop, for the first time, a rigorous energy landscape approach capable of reproducing trends observed in simulations, in particular, the temperature dependence of the energy and fractional order of sampled saddles.

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In recent years significant effort has been devoted to the study of supercooled liquids and their glasses [1]. An important aspect of these technologically significant [2] systems is the interplay between dynamic and thermodynamic processes, which is thought to play a key role in their kinetic slowdown and eventual falling out of equilibrium at the glass transition [3]. The energy landscape formalism of Stillinger and Weber has been a useful tool in the theory of supercooled liquids [4]. In this description, a system's configuration space is partitioned into basins surrounding local energy minima. Termed "inherent structures," these minima correspond to mechanically stable particle packings and are described statistically by their depth:  $\exp[N\sigma(\phi)]d\phi$  gives the scaling of the number of distinct minima with per-particle potential energy (or depth)  $\phi \pm d\phi/2$ , where  $N$  is the number of particles and  $\sigma$  is called the basin enumeration function (implicitly density dependent). Here, "distinct" refers to minima differing by more than mere particle permutation. This formalism permits a rigorous transformation of the canonical partition function,

$$Z \sim \int e^{N[\sigma(\phi) - \beta\phi - \beta a_{\text{vib}}(\beta, \phi)]} d\phi, \quad (1)$$

where  $\beta = 1/k_B T$  and  $a_{\text{vib}}$ , the vibrational free energy, is the per-particle free energy when the system is confined to an average basin of depth  $\phi$  at the given density. For each temperature in the thermodynamic limit, the system samples basins of a well-defined energy  $\phi^*$ ; deeper basins are accessed as the temperature decreases. One identifies a configurational entropy,  $Nk_B\sigma(\phi^*)$ , which is that part of the entropy due to the multiplicity of amorphous configurations explored by the system. Good functionalities can be rationalized for  $\sigma$  and  $a_{\text{vib}}$  (and measured in computer simulations) such that the partition function can be explicitly evaluated [5]; this approach is also useful for characterizing kinetic processes as it has been observed that the configurational entropy plays a key role in dynamics [3,6].

Our work aims to extend the energy landscape formalism to include a description of higher order stationary points, i.e., saddles in the landscape [7]. This approach provides a natural connection with dynamics [8,9], but is more intricate than minima alone because, in addition to their energy, saddles are also classified by their order—the number of directions with negative curvature. In this Letter, we begin by deriving the extensivity properties of saddles and propose their corresponding enumeration function. We then derive a saddle "equipartition" theorem and show the expected scaling behavior for low-order saddles. Finally, we give the appropriate form of the partition function in this formalism and demonstrate its utility for describing the behavior of supercooled liquids.

Our consideration of saddles relies on an extensive macroscopic potential energy, i.e., that a macroscopic system of  $N$  particles can be effectively divided into  $M \ll N$  equivalent subsystems with negligible boundary interactions. The number of particles in each subsystem is macroscopic,  $N_S \gg 1$ , but the number of subsystems is also large,  $N_S \ll N$ . This condition is satisfied by most common types of molecular interaction (notable exceptions include molecules with long-range interactions or which are themselves macroscopic in size). For a single-component system of structureless particles, the potential energy can then be written as

$$U(\mathbf{r}^N) \approx U(\mathbf{r}_{(1)}^{N_S}) + U(\mathbf{r}_{(2)}^{N_S}) + \dots + U(\mathbf{r}_{(M)}^{N_S}), \quad (2)$$

where  $U$  is the potential energy function,  $\mathbf{r}^N \equiv \{\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N\}$  gives the positions of the particles, and  $\mathbf{r}_{(i)}^{N_S}$  are the corresponding positions of the  $N_S$  particles in subsystem  $i$ . Here, any stationary point in the overall system can be viewed as a combination of stationary points in each subsystem. It is straightforward to determine the scaling behavior of minima [10]: if the number of distinct minima in each subsystem is  $g_0$ , the total number due to their possible combinations is  $g_0^M$ , or  $\exp[N \ln(g_0)/N_S] \equiv \exp[N\sigma_\infty]$  [11]. Our notation for the density-dependent constant  $\sigma_\infty$  indicates its

correspondence with the total number of inherent structures (not of a particular energy); equivalently,  $\sigma_\infty$  is the maximum value of the basin enumeration function.

For saddles, one must consider their order  $n$ , the number of negative eigenvalues in the Hessian matrix,  $H_{ij} \equiv \partial^2 U / \partial r_i \partial r_j$ . Imposition of Eq. (2) gives rise to a Hessian which is reducible in each of the subsystems; therefore, the total number of negative eigenvalues is the sum of that for each of the subsystems. In other words, the saddle order in the total system is the sum total of the orders of the subsystems. We consider a particular distribution of the total saddle order  $n$  among the subsystems, letting  $M_i$  be the number of subsystems containing saddles of order  $i = 0, 1, \dots, dN_S$  ( $d = \text{dimensionality}$ ). In this notation, the constraints are  $\sum_i M_i = M$  and  $\sum_i i M_i = n$ . For an overall saddle order  $n$  and a particular distribution  $\{M_i\}$ , the number of distinct saddles is

$$\Omega_n(\{M_i\}) = \left( M! / \prod_i M_i! \right) \prod_i g_i^{M_i}, \quad (3)$$

where  $g_i$  is the number of distinct saddles of order  $i$  in a subsystem. The total number of saddles, however, must be the sum of  $\Omega_n(\{M_i\})$  for all possible distributions  $\{M_i\}$ . We will find that one particular distribution,  $\{M_i\}_{\max}$ , overwhelmingly dominates this sum. First, we switch to an ‘‘intensive’’ notation by introducing the following variables:  $m_i \equiv M_i/M$ , and  $x \equiv n/dN$  is the overall fractional saddle order. Insertion into Eq. (3) and application of Stirling’s approximation yields

$$\Omega_x(M, \{m_i\}) = \left[ \prod_i (g_i/m_i)^{m_i} \right]^M. \quad (4)$$

Similarly, the constraint equations in intensive form become  $\sum_i m_i = 1$  and  $\sum_i (i/dN_S)m_i = x$ . These constraints and the terms inside the brackets in Eq. (4) are all independent of the number of subsystems  $M$ . As a result, the distribution  $\{m_i\}_{\max}$  which maximizes the term in brackets depends only on the overall fractional saddle order  $x$ . In the thermodynamic limit,  $M = N/N_S \rightarrow \infty$ , this maximum term dominates the sum over all distributions  $\{m_i\}$ . These considerations lead directly to the saddle scaling behavior:

$$\Omega_x(N) = \left[ \prod_i (g_i/m_i)^{m_i} \right]_{\max}^{N/N_S} \equiv \exp[N\theta_\infty(x)], \quad (5)$$

where  $\Omega_x$  gives the number of distinct saddles of fractional order  $x$ . Here, we have introduced the generalized function  $\theta_\infty(x)$  which characterizes saddle scaling behavior and has the property  $\theta_\infty(x \rightarrow 0) = \sigma_\infty$ . Notice that the relevant order parameter for saddles is their fractional order, such that  $\exp[N\theta_\infty(x)]dx$  gives the number of saddles with fractional order  $x \pm dx/2$ .

Returning to the subsystem scenario, we now find the distribution  $\{m_i\}_{\max}$  which gives the dominant saddles in

the system. To do so, one maximizes the term in brackets in Eq. (4) or, equivalently, its logarithm. By accounting for the constraints with the usual Lagrange multipliers and using Eq. (5) for  $g_i = \exp[N_S\theta_\infty(i/dN_S)]$ , the following result is obtained:

$$m_i = \frac{\exp[N_S\theta_\infty(z_i) - \gamma z_i]}{\sum_{i'} \exp[N_S\theta_\infty(z_{i'}) - \gamma z_{i'}]}, \quad (6)$$

where  $z_i \equiv i/dN_S$  is the fractional order of a subsystem. Here  $\gamma$  is a Lagrange multiplier ensuring the constraint  $\sum_i z_i m_i = x$ . Because the terms in the exponential grow with the size of the subsystems, which are themselves macroscopic,  $m_i$  is essentially zero for all  $i$  except one,  $i_{\max}$ . With this simplification, the constraint yields  $i_{\max} = n/M$ , or  $z_{\max} = x$ . In other words, the total saddle order is distributed across the subsystems such that their fractional saddle order is equivalent to each other and to the overall fractional order. This is in effect an equipartition of saddle order across the geometry of the system.

Such equipartition has important consequences for low-order saddles; it implies that the majority are built from a collection of localized first-order saddles. In this sense, each direction of negative curvature in the potential energy corresponds to an elementary saddle ‘‘defect’’ in an inherent structure. This observation can be used to determine the approximate behavior of  $\Omega_x$  for small values of  $x$ . Assuming that  $\xi dN$  noninteracting, first-order defects are possible for any inherent structure, where  $\xi$  is  $N$  independent,

$$\Omega_{x \ll 1} \sim \exp[N\sigma_\infty](\xi dN)! / (\xi dN - xdN)!(xdN)!. \quad (7)$$

The combinatorial term accounts for the number of ways of picking  $xdN$  independent diffusive directions from the  $\xi dN$  available. Taking the logarithm and applying Stirling’s approximation,

$$\theta_\infty(x \ll 1) \approx \sigma_\infty - dx \ln \frac{x}{\xi} - d(\xi - x) \ln \left( 1 - \frac{x}{\xi} \right). \quad (8)$$

It follows that for a system containing noninteracting first-order saddles that the average saddle energy depends linearly on order:  $\bar{\Phi}_n = \bar{\Phi}_0 + n(\bar{\Phi}_1 - \bar{\Phi}_0)$ , where  $\bar{\Phi}_n$  is the average energy of an  $n$ th order saddle. This trend has been discussed previously in theoretical work [7] and has been found in simulation studies to be appropriate [12,13]. One must bear in mind, however, that this behavior and the equipartition of saddles apply to the entire ensemble of stationary points, of which only a minute fraction are sampled at low temperature. A system may require, for example, the cooperative movement of many molecules in order to reach nearby saddles, which may necessitate high-order, low-energy stationary points. If the low- $T$  linear relationship between saddle order and energy observed in simulation is, indeed, the result of a first-order defect scenario, then cooperativity arises

because the direction of negative potential energy curvature about these points is a superposition of several molecules' atomic coordinates.

The considerations so far have categorized saddles only by their fractional order. Following the approach used for inherent structures [4], one might extend this description to potential energy. We therefore introduce the saddle enumeration function,  $\theta(\phi, x)$ , for which the expression  $\exp[N\theta(\phi, x)]d\phi dx$  is proportional to the number of saddles with potential energy per-particle  $\phi \pm d\phi/2$  and of fractional order  $x \pm dx/2$  [14]. [The basin enumeration function is retrieved from  $\theta(\phi, x = 0)$ .] This extension allows a meaningful casting of the canonical partition function in which configuration space is divided into "basins" surrounding saddle points [15]:

$$Z \sim \int_{x=0}^{x=1} \int_{\phi_{\min}}^{\phi_{\max}} e^{N[\theta(\phi, x) - \beta\phi - \beta a_{\text{vib}}(\beta, \phi, x)]} d\phi dx. \quad (9)$$

In this equation,  $a_{\text{vib}}$  is the vibrational free energy around a stationary point of energy  $\phi$  and fractional order  $x$ ; formally it is given by

$$e^{-\beta N a_{\text{vib}}(\beta, \phi, x)} \equiv \Lambda^{-dN} \left\langle \int_{\Gamma_k} e^{-\beta[U(\mathbf{r}^N) - N\phi]} d\mathbf{r}^N \right\rangle_{\phi, x}, \quad (10)$$

where  $\Lambda$  is the thermal de Broglie wavelength, the average is restricted to saddle points of energy  $\phi$  and order  $x$ , and the integral for a particular saddle  $k$  is performed over its associated configuration space  $\Gamma_k$  [15]. In the large system limit, the integral in Eq. (9) is dominated by the maximum in the exponential, and the conditions for equilibrium can be written as

$$\frac{\partial \theta}{\partial \phi} = \beta \left( 1 + \frac{\partial a_{\text{vib}}}{\partial \phi} \right); \quad \frac{\partial \theta}{\partial x} = \beta \frac{\partial a_{\text{vib}}}{\partial x}. \quad (11)$$

The simultaneous solution to these equations provides the average saddle energy  $\phi^*$  and order  $x^*$  sampled by the system at specified temperature. The total Helmholtz free energy is then  $A/N = a_{\text{vib}}(\beta, \phi^*, x^*) + \phi^* - k_B T \theta(\phi^*, x^*)$ . One can identify from this equation a per-particle saddle entropy,  $k_B \theta$ , which converges on the conventional Stillinger-Weber configurational entropy at very low temperatures when the system spends most of its time near minima and  $x^*$  asymptotes to zero. This point of view sets the stage for a more rigorous connection with dynamics, for which  $x^*$  contains pertinent information.

The functions  $\theta$  and  $a_{\text{vib}}$  completely determine the system thermodynamics. We now show that reasonable assumptions about their functional form result in a physically realistic and insightful picture. Our analysis addresses results for a well-studied, binary glass former for which numerical data exist [9,12,13,16,17]. First, we assume the vibrational free energy to be independent of saddle energy,  $a_{\text{vib}}(\beta, \phi, x) \approx a_{\text{vib}}(\beta, x)$ . This is rigorously true for minima at absolute zero, but remains a working simplification in our analysis. Furthermore, we

model the vibrational free energy in the classical harmonic approximation [18]:

$$e^{-\beta N a_{\text{vib}}} \approx \Lambda^{-dN} \left[ \int_{-l}^l e^{-\beta \alpha_S r^2} dr \right]^{dN-n} \left[ \int_{-l}^l e^{\beta \alpha_U r^2} dr \right]^n, \quad (12)$$

$$\begin{aligned} \beta a_{\text{vib}} &\approx d \ln(T_S^{1-x} T_U^x / T) - x \ln \operatorname{erfi} \sqrt{\beta \alpha_U l^2} \\ &\approx d \ln(T_S / T) - x [C\beta - \ln(\pi C\beta) / 2], \end{aligned} \quad (13)$$

where  $\alpha_S, \alpha_U \equiv \frac{1}{2} |\frac{\partial^2 U}{\partial r^2}|$  are half the geometric mean curvatures of stable and unstable modes, respectively;  $T_S$  and  $T_U$  are the corresponding Einstein temperatures [18];  $l$  is a length scale characteristic of the saddle's associated configuration space volume [19]; and  $\operatorname{erfi}$  is the imaginary error function. Here, the small contribution from the stable-mode error function has been neglected. In the last line, we assume  $\alpha_S = \alpha_U$  and use the asymptotic expansion of the error function,  $\operatorname{erfi}(x) \rightarrow \exp[x^2]/x\sqrt{\pi}$ , for the low  $T$  limit.  $C = \alpha_U l^2$  is a lumped constant. In general, the harmonic approximation is increasingly valid for stable modes at low temperatures, but we have made liberal use of its application to the unstable modes, especially in that the final  $a_{\text{vib}}$  depends nontrivially on the length scale  $l$  characterizing the  $dN$ -dimensional integral. Nonetheless, this approximation provides a starting point for analysis, and we leave investigation of more accurate forms to future work.

For the saddle enumeration function, we assume a Gaussian form in energy, consistent with previous simulation studies [9,17,20,21]:

$$\theta(\phi, x) = \theta_{\infty}(x) [1 - (\phi - \bar{\phi}(x))^2 / \Delta^2], \quad (14)$$

where  $\bar{\phi}$  is the midpoint energy of saddles of fractional order  $x$  and  $\Delta$  is their characteristic energy range. For the dependence of the parameters in this expression on fractional saddle order, we use Eq. (8) for  $\theta_{\infty}$ , implement the low-order linear relationship for  $\bar{\phi}$  such that  $\bar{\phi}(x) = \bar{\phi}_0 + \delta x$ , and assume  $\Delta$  to be roughly constant.

The usefulness of this approach can be seen in the predictions of the theory. Such an analysis is possible by solving Eq. (11) with the simplified expressions for the vibrational free energy and the saddle enumeration function. We choose representative parameters based on previous simulations [22]. The results in Fig. 1 demonstrate that the theory and assumptions capture the low- $T$  behavior observed in simulations and are a promising starting point for the approach. We observe some flexibility in the choice of the fitted parameters, though these might readily be investigated in detail by a future simulation study.

In summary, we have presented a thermodynamic formalism which includes higher order stationary points in the energy landscape. Through a reformulation of the canonical partition function and by using several physically motivated simplifications, we show that this

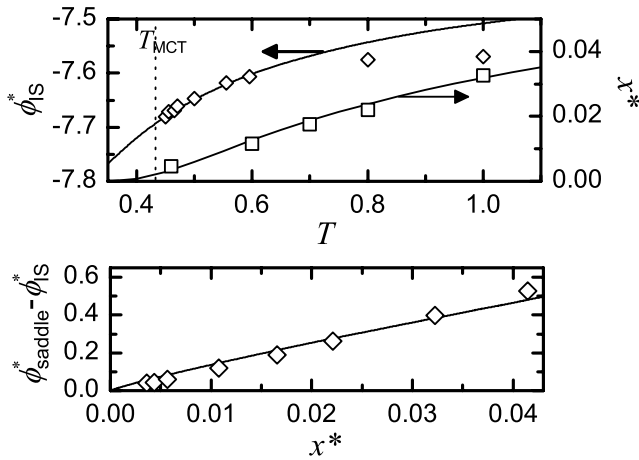


FIG. 1. (Top) Plot of the equilibrium inherent structure energy and fractional saddle order. The lines are the predictions of the theory and the symbols are the respective results for a binary Lennard-Jones system [12,23]. The theoretical  $x^*(T)$  curve approaches zero near  $T_{\text{MCT}} \approx 0.435$ , the mode-coupling temperature [16], but remains finite until absolute zero. (Bottom) Corresponding plot of saddle elevation energy as a function of equilibrium saddle order.

formalism captures important trends in the behavior of low- $T$  glass-forming materials. Future work will investigate the relationship suggested by this approach between liquid kinetics and thermodynamics.

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