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Why is the density of inherent structures of a Lennard-Jones-type system Gaussian?

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Abstract. The thermodynamics of glass-forming systems can be expressed in terms of the density of inherent structures, which correspond to the minima of the potential energy landscape. In previous work this approach has been applied to Lennard-Jones-type systems, yielding a density of inherent structures which to a very good approximation turned out to be Gaussian. In this work we clarify whether the Gaussian distribution is just a consequence of the central-limit theorem or whether it also contains information about the local structure of the glass-forming system.

1. Introduction

For understanding the physics of glass-forming systems it has proven to be helpful to analyse their potential energy landscape [1–3]. The dynamics of the total system can be viewed as the dynamics of a single point in configuration space, moving in the potential energy landscape. According to a picture suggested, e.g., by Goldstein and Stillinger the potential energy landscape can be formally divided into basins of attraction of the different local energy minima (inherent structures, IS). These basins of attraction are separated by saddle points. At sufficiently low temperatures, the timescale of intra-basin motion starts to exceed the timescale of inter-basin motion by many orders of magnitude, so the overall relaxation is mainly determined by saddle crossing. For a Lennard-Jones system it can be shown that this separation of timescales takes place for a temperature close to the critical mode-coupling temperature [4]. Very recently, several interesting features of the potential energy landscape of structural glass formers have been elucidated [5–10]. Also, analytical treatment is possible [11, 12].

Formally the configurational contribution to the total partition function can be written as

$$Z(T) = \int \mathrm{d}\epsilon\; z(\epsilon, T) \tag{1}$$

with

$$z(\epsilon, T) = \exp(-\beta\epsilon) G(\epsilon) z_{basin}(\epsilon, T) \tag{2}$$

where $G(\epsilon)$ denotes the density of IS, β the inverse temperature and $z_{basin}(\epsilon, T)$ the average partition function of a basin of attraction related to an IS with energy ϵ. The scenario described above for low temperatures implies that the system resides nearly exclusively close to the inherent structures. Therefore the thermodynamics of the system is related to properties of the minima. Formally this is expressed by the fact that $z_{basin}(\epsilon, T)$ is mainly determined by the energy of the IS as well as the harmonic force constants, i.e. $z_{basin}(\epsilon, T) \approx z_{harm}(\epsilon, T)$ where the latter is the harmonic approximation, only involving the second derivatives ν_i of the potential energy, evaluated for the respective IS, i.e.

$$z_{harm}(\epsilon, T) = \exp(-\beta\epsilon) y_{harm}(\epsilon) \tag{3}$$

with

$$y^{harm}(\epsilon) \equiv \left\langle \prod (2\pi/\nu_i)^{0.5} \right\rangle. \tag{4}$$

For reasons of simplicity we neglect a possible temperature dependence of $y^{harm}(\epsilon)$ (see reference [9] for details).

In principle, information about $G(\epsilon)$ can be obtained by systematic determination of all IS [13–18]. Since the number of IS increases exponentially with system size this is not possible for relevant system sizes (approximately $N > 40$ for a monatomic Lennard-Jones system). A different approach to elucidating properties of the IS is to perform equilibrium MD (or MC) simulations at temperature T and to regularly quench the system, i.e. find the nearby minimum of the potential energy, thus probing properties of the IS accessible at this temperature [3,13,19]. The probability $P(\epsilon, T)$ of finding an IS with energy ϵ with this algorithm is given by

$$P(\epsilon, T) = z(\epsilon, T)/Z(T). \tag{5}$$

Very recently, this approach has been used to analyse the thermodynamics of binary Lennard-Jones systems [7, 8] and a spin-glass system [20]. The primary results of the simulations of structural glass formers can be expressed as the density of IS, i.e. $P(\epsilon, T)$, and the average phase space of the IS in the harmonic approximation as expressed by $y^{harm}(\epsilon)$. If $y^{harm}(\epsilon)$ does not depend on ϵ, one simply has (combining equations (2) and (5))

$$G(\epsilon) \propto P(\epsilon, T) \exp(\beta\epsilon) \tag{6}$$

with a constant of proportionality which only depends on temperature. Therefore apart from a normalization constant, $G(\epsilon)$ can be simply recovered from knowledge of $P(\epsilon, T)$. Since for a given temperature only a small fraction of the total energy range is probed, this analysis has to be repeated for different temperatures and the different resulting curves have to be shifted with respect to each other in order to yield an optimum overlap. In this way the ϵ-dependence of $G(\epsilon)$ can be determined for a large ϵ-range. As explicitly shown in reference [9], a perfect overlap of the curves obtained at different temperatures is also possible if the harmonic force constants, i.e. $y^{harm}(\epsilon)$, depend on the energy. The resulting curve, however, is no longer the density of IS $G(\epsilon)$ but rather the effective density $G_{eff}(\epsilon) \equiv G(\epsilon) y^{harm}(\epsilon)$. It is the latter quantity which is relevant for the thermodynamics. The scaling breaks down at high temperatures where the harmonic approximation is no longer valid.

2. Simulations

For a model Lennard-Jones-type system we have performed simulations along the lines described above and obtained the effective density $G_{eff}(\epsilon)$ for different system sizes. Details of the model and the simulations are described in reference [9]. We systematically varied the system size between $N = 20$ and $N = 160$ and the temperature between $T = 2.5$ and $T = 0.667$ (the mode-coupling critical temperature for this model can be estimated to be 0.56 [9,21]). Whereas the systems with size $N = 20$ and $N = 40$ display significant finite-size effects, the larger systems ($N \geqslant 60$) are devoid of major finite-size effects in this temperature range. In figure 1 we display the energy dependence of $G_{eff}(\epsilon)$ for $N = 60$ and $N = 120$. The different parts of the curve, obtained for the different temperatures, scale very well for the three

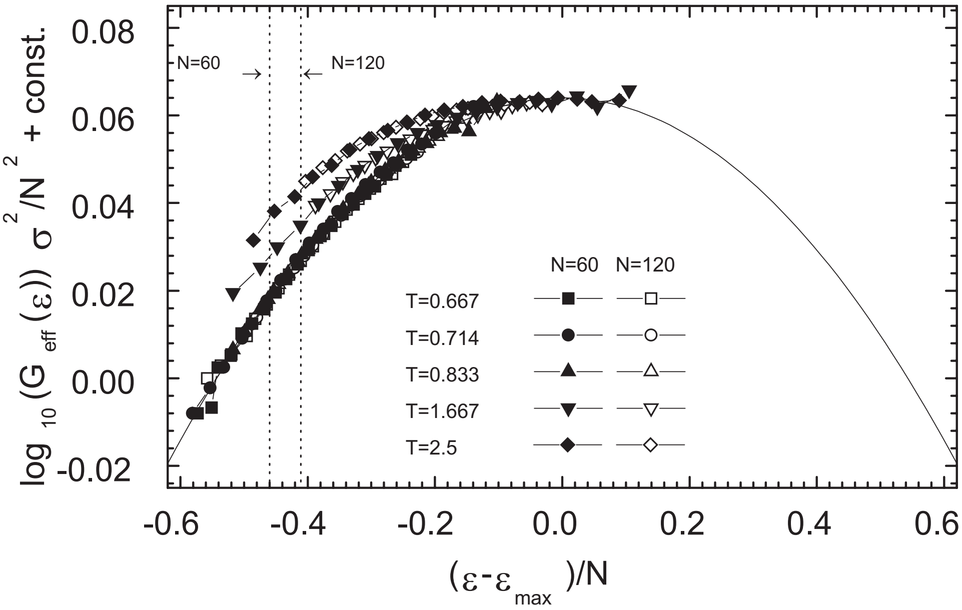

Figure 1. Determination of $G_{eff}(\epsilon)$ on the basis of $P(\epsilon, T)$ for $N = 60$ and $N = 120$. The individual curves have been shifted in order to obtain an optimum overlap. The representation is such that the fitted Gaussian function has its maximum at zero and a variance of one. The values of ϵ_{max} and σ for both N-values are given in the text.

lowest temperatures, whereas the scaling breaks down for the two higher temperatures. In any event, $G_{eff}(\epsilon)$ is very well defined for a large energy range. To a very good approximation, for both system sizes $G_{eff}(\epsilon)$ can be fitted very well by a Gaussian distribution with a maximum for $\epsilon = \epsilon_{max}$ and variance σ^2. From harmonic fits of $\log G_{eff}(\epsilon)$ we obtain $\epsilon_{max}/N = -5.61$ and $\sigma^2/N = 0.3$ for $N = 60$ and $\epsilon_{max}/N = -5.65$ and $\sigma^2/N = 0.27$ for $N = 120$. In figure 1 an appropriate normalization of the two curves has been chosen such that the two curves agree perfectly.

As extensively discussed in reference [9], the thermodynamics in the high-temperature regime ($T = 1.66, 2.5$) is dominated by anharmonic contributions, i.e.

$$z^{anh}(\epsilon, T) \equiv z(\epsilon, T)/z_{harm}(\epsilon, T) \neq 1$$

so the scaling breaks down. Interestingly, for the three lower temperatures also the analysis of the specific heat has clearly revealed the presence of anharmonic contributions [9]. If, however, $z^{anh}(\epsilon, T)$ only shows a very weak ϵ-dependence, these anharmonic contributions scale out in the construction of $G_{eff}(\epsilon)$. Obviously, this is the case for our system. We note that the ϵ-dependence of $y^{harm}(\epsilon)$ is rather weak, so $G_{eff}(\epsilon) \approx G(\epsilon)$ [7,9].

Furthermore, we have determined the variance $\sigma_P^2(T)$ of $P(\epsilon, T)$. The results are shown in figure 2 (here also for different values of N in addition to 60 and 120). Again, the data at the two higher temperatures are dominated by anharmonic contributions. The important observation is that apart from statistical variations the variance does not show a systematic trend at lower temperatures. It is easy to check that for a purely Gaussian distribution one expects $\sigma_P^2(T) = \sigma^2 = \text{constant}$. Furthermore, one has to a good approximation $\sigma_P^2 \propto N$ in the limit of large system sizes.

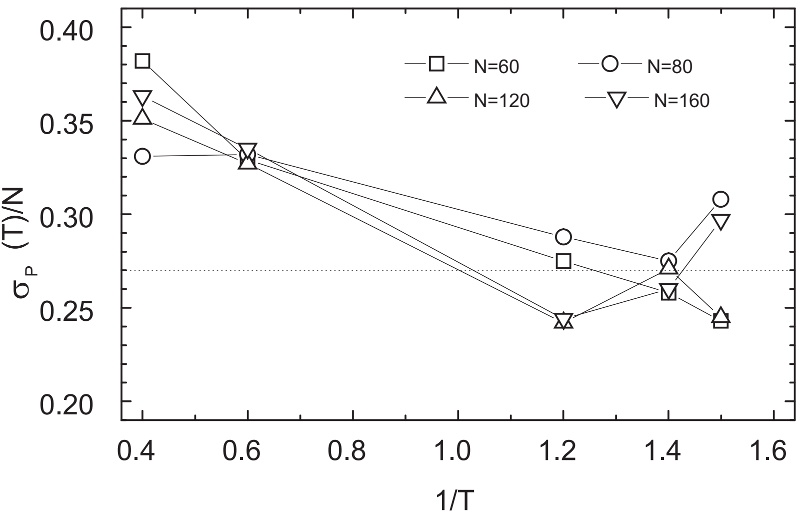

Figure 2. The variance $\sigma_P^2(T)$ of $P(\epsilon, T)$ calculated for different temperatures and system sizes between $N = 60$ and $N = 160$.

3. Why Gaussian?

After examining the results of our simulation, one may ask to what degree the Gaussian behaviour of $G_{eff}(\epsilon)$ is just a consequence of the central-limit theorem or reflects information about the distribution of energies of inherent structures. In the following analysis we will end up with an upper bound for the non-Gaussian parameter α_2 of the elementary distribution which describes the energy of the IS on a local scale. The meaning of the elementary distribution will be discussed further below. We derive two different criteria for estimating an upper bound for α_2. First, we explicitly calculate the deviations of $G_{eff}(\epsilon)$ from a Gaussian in first order. Second, we analyse the temperature dependence of the variance of the distributions $P(\epsilon, T)$. At the end we discuss the sensitivity of the two criteria.

3.1. Modified Gaussian distribution

We consider a probability variable y which is composed of M independent probability variables x_i, i.e.

$$y = \sum_{i=1}^{M} x_i. \tag{7}$$

The x_i are characterized by the same distribution $r(x)$. For reasons of simplicity we assume that $r(x)$ is symmetric around $x = 0$. Later on we identify y with the total potential energy of the inherent structures and x_i with the local contribution to the potential energy. The following analysis of non-Gaussian effects is similar to the derivation of the central-limit theorem. The total distribution function $p(y)$ can be written as

$$p(y) = \int \mathrm{d}x_1 \cdots \mathrm{d}x_M \; p(x_1) \cdots p(x_M) \delta\left(y - \sum_{i=1}^{M} x_i \right). \tag{8}$$

Using the standard tricks of rewriting the δ-distribution and introducing the variable $z = y/\sqrt{M}$ one finally ends up with

$$p(z) \propto \int \mathrm{d}q \ \exp(-\mathrm{i}qz) \left\{ \int \mathrm{d}x \ r(x) \exp(\mathrm{i}qx/\sqrt{M}) \right\}^M . \tag{9}$$

Rewriting the bracketed term $\{\cdots\}^M$ as $\exp M \ln\{\cdots\}$, the logarithm can be expanded in inverse powers of M, yielding

$$p(z) \propto \int \mathrm{d}q \ \exp(-\mathrm{i}qz) \exp[-s^2q^2/2 + \alpha_2 s^4 q^4/8M + \mathrm{O}(M^{-2})] \tag{10}$$

with the variance

$$s^2 \equiv \langle x^2 \rangle \tag{11}$$

and the non-Gaussian parameter

$$\alpha_2 \equiv \frac{\langle x^4 \rangle - 3s^4}{3s^4} \tag{12}$$

where the average is over the elementary distributions $r(x)$. Note that one has $\sigma^2 = Ms^2$. For large M the final term can be expanded and the integration over q can be performed. This results in

$$p(z) \propto \exp[-z^2(1 + 3\alpha_2/M)/2s^2 + \alpha_2 z^4/8Ms^4 + \mathrm{O}(M^{-2})]. \tag{13}$$

Rewriting this expression again in terms of y, and identifying y with the total potential energy ϵ, one obtains for large M

$$G_{eff}(\epsilon) \propto \exp\{-M[((\epsilon - \epsilon_{max})/M)^2/2s^2 + \alpha_2((\epsilon - \epsilon_{max})/M)^4/8s^4]\}. \tag{14}$$

For a Gaussian distribution the average value of the energy of IS $\langle\epsilon\rangle_T$ at temperature T is given by

$$\langle\epsilon\rangle_T = \epsilon_{max} - \frac{\sigma^2}{T}. \tag{15}$$

The ratio of the fourth-order and the second-order terms of $\log(G_{eff}(\epsilon))$ evaluated for $\epsilon = \langle\epsilon\rangle_T$ is given by

$$\frac{\alpha_2 s^2}{4T^2}. \tag{16}$$

In the case where at a given temperature T the deviations of a quadratic fit of $\log(G_{eff}(\epsilon))$ are less than δ_g at $\epsilon = \langle\epsilon\rangle_T$, one obtains an upper bound for α_2 via

$$|\alpha_2| < 4\delta_g(T/s)^2. \tag{17}$$

Application of equation (17) requires that the determination of the quadratic term of $\log(G_{eff}(\epsilon))$ is performed around $\epsilon \approx \epsilon_{max}$ where non-Gaussian corrections are irrelevant. Unfortunately, in exactly this region the effective density is only poorly defined. The reason is that IS with energy $\epsilon \approx \epsilon_{max}$ are only visited at high temperature, so their quantification is always hampered by the presence of anharmonic effects; see figure 1. Therefore we present a second criterion which does not require any fitting.

3.2. Variance of $P(\epsilon, T)$

Another upper bound for α_2 can be obtained from analysis of the variance of $P(\epsilon, T)$, i.e. $\sigma_p^2(T)$. Using the first and second moment ($n = 1, 2$),

$$A_n(T) \equiv \left(\int_0^\infty \mathrm{d}x\; x^n r(x) \exp(-\beta x)\right) \Big/ \left(\int_0^\infty \mathrm{d}x\; r(x) \exp(-\beta x)\right) \tag{18}$$

we can define the temperature dependence of the variance $s^2(T)$ via

$$s^2(T) \equiv A_2(T) - A_1(T)^2. \tag{19}$$

Then a straightforward calculation yields via a high-temperature expansion

$$s^2(T) = s^2 + \frac{3\alpha_2 s^4}{2T^2} \tag{20}$$

which is related to $\sigma_p^2(T)$ via

$$\sigma_p^2(T) = Ms^2(T). \tag{21}$$

For finite α_2 one expects that, in cooling, the value of $\sigma_p^2(T)$ is constant at high temperatures and changes at lower temperatures. From the observation that

$$|\sigma_p^2(T) - \sigma_p^2(T = \infty)|/\sigma_p^2(T = \infty) < \delta_p$$

one can again derive an upper limit for the non-Gaussian parameter:

$$|\alpha_2| < (2/3)(T/s)^2 \delta_p. \tag{22}$$

Note that $\sigma_p^2(T = \infty)$ denotes the variance that one would have at infinite temperature without any anharmonic contributions.

3.3. General remarks

Before application for numerical data one has to specify the meaning of the elementary distribution and thus of M. The value of M is of importance for the present analysis since the value of s^2 has to be determined from the numerically accessible value of σ^2 via $s^2 = \sigma^2/M$. If the particles were not interacting (think of a spin model without spin–spin interaction), $r(x)$ would be directly identified with the single-particle energy distribution and $M = N$. For structural glasses (as well as for spin glasses) one expects the energy of adjacent particles to be no longer uncorrelated, with the result that the elementary level corresponds to small regions, containing a few particles, rather than single particles, implying $M < N$. Due to the disorder, these energetically correlated regions are probably rather small. In what follows we will choose $M = N$. This choice implies that the estimate of the upper bound for α_2 that we will obtain is too conservative in the case of significant spatial energy correlations.

4. Analysis of simulated data

Here we explicitly analyse that data for $N = 60$ and $N = 120$. One clearly observes that within statistical noise no systematic trend is present which would indicate the presence of non-Gaussian effects. A conservative estimate is that $\log(G_{eff}(\epsilon))\sigma^2/N^2$ deviates by at most 0.002 from the fitted parabola evaluated at $\epsilon = \langle\epsilon\rangle_T$ (the broken line in figure 1). This yields $\delta_g = 0.002/0.044 = 0.045$ and $\delta_g = 0.002/0.037 = 0.054$ for $N = 60$ and $N = 120$, respectively. Application of equation (17) for the lowest temperature then yields $|\alpha_2| < 0.3$.

For application of the second criterion we first have to specify to which level the variance does not change with temperature. On the basis of the statistical uncertainties one can estimate

$\delta_p < 0.2$. Application of equation (22) then yields $|\alpha_2| < 0.2$. As discussed above, the second estimate is more reliable since no fitting is involved. Averaging the data for different N the statistical error would be even smaller, resulting in a smaller upper bound for $|\alpha_2|$.

It may be interesting to compare our results with the extreme case of a bimodal distribution of local energies, corresponding to the presence of solid-like and liquid-like regions with local energies E_s and E_l, respectively, expressed by

$$r(x) = p_s\delta(x - E_s) + (1 - p_s)\delta(x - E_l).$$

At high temperatures it will be much more likely to have a liquid-like configuration, which implies $p_s \ll 1$. In this limit one obtains $\alpha_2 = 1/(3p_s) \gg 1$. Obviously, our numerical results are not compatible with this kind of model. A formal analysis of this model would also involve additional correction terms since $r(x)$ is no longer symmetric. These terms, however, would render the discrepancy even larger. Conversely, one can state that for systems characterized by sufficiently large values of α_2, it is indeed possible to observe strong deviations from a purely Gaussian behaviour. For $\alpha_2 = 1$ one would for example expect $\sigma^2(T = 0.667)$ to have changed by as much as a factor of two as compared to its value at high temperatures.

In summary, the large degree of Gaussianity, observed in recent simulations of Lennard-Jones systems, is only partly due to the central-limit theorem and also contains important information about the properties the glass-forming system on a local level; it may, for the present system, render inapplicable some models which involve large non-Gaussian effects on a local scale.

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