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Asymptotic universality in the vibrational spectra of amorphous single-component systems

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We have numerically investigated the vibrational spectra of bulk single-component systems for which the potential energy depends only on the positions of the constituent units and is of the form of a sum over pairs. When the width of the potential well describing the two-body interaction is reduced progressively, our results suggest that the shape of the entire spectrum in the amorphous state approaches a limit that is independent of the explicit functional form of the potential. We use this observation of asymptotic universality to explain the quasiuniversal nature of vibrational spectra that has been observed in recent experimental studies of bulk molecular glasses [Chumakov *et al.*, Phys. Rev. Lett. **92**, 245508 (2004)].

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I. INTRODUCTION

Vibrational spectra of solids have been studied for several decades now owing to their immediate value in unraveling the nature of the interaction among the constituent units. Although the earliest studies were concerned with crystalline systems, in more recent times a large amount of attention has been focused on disordered solids and some rather generic features have been discovered—the presence of a "boson peak" being one example.[1–16] However, these generic features are typically qualitative in nature and there exist few quantitatively precise universal properties. One exception is the fluctuation properties of the spectra where ideas of random matrix theory have been demonstrated to be applicable and it is found that spectral fluctuations are universally described by one of only a few types of possibilities.[12,17–20] However, the pattern of variation in a sequence of interlevel spacings in a spectrum has a smoothly varying part and a rapidly fluctuating part. It is only the latter aspect that is addressed by the theories of spectral fluctuations. For bulk systems what is more relevant for experimental purposes is the smoothly varying part of the interlevel spacing, which is controlled by the density of states (DOS) function. Hence in this paper we address the following question: For the amorphous state are there any situations in which even the DOS function is amenable to universal description? Since the vibrational spectrum is determined by the underlying geometry and interactions, superficially the only situation in which even broad commonality may be expected between the spectra of different systems is when the systems are crystalline and have identical crystalline features. For amorphous systems there are no such obvious grounds. Hence the answer to the question posed above would seem to be in the negative. Yet two recent sets of studies, one involving experiments on bulk glasses[15,16] and the other involving computational studies on models of simple single-component amorphous clusters,[17] have found that the DOS function has a near-universal shape over a large central part of the spectrum. The main purpose of this paper is to present numerical results for model potentials which suggest that underlying the approximate universality that has been observed in these studies is an exact universality that extends over the entire vibrational spectrum in some generic limiting situations that are obtained by suitably varying the parameters of the potentials. The asymptotic forms of these potentials do not describe any realistic physical systems. But, by virtue of being proximate in property to ones that are realistic, they help us understand the properties of the latter cases. It has been demonstrated repeatedly over the last few decades that, while universality is not a common occurrence in physics, empirical observation of its presence has often provided the seed for significant progress in theoretical efforts. In the present case the existence of universality might make the seemingly impossible task of analytically calculating the vibrational spectrum *ab initio* for the amorphous state more tractable for certain types of interactions. In Sec. II of this paper we describe the methodology and results of our investigation. Section III contains the discussion and some concluding remarks.

II. METHODOLOGY AND RESULTS

We first describe how stable and disordered solid configurations are generated. For this purpose we assume that the potential energy of the system is determined solely by the position vectors of the constituent units (atoms or molecules) and is of the form of a sum over pairs. We choose a model for the pair potential and then generate stable periodic structures in which the number of constituent units per unit cell is N. To produce a state with finite disorder the value of N should ideally be infinite. In practice the maximum value of N is controlled by computational resources. In our case $N=343$ unless otherwise stated. If $\vec{a}$, $\vec{b}$, and $\vec{c}$ denote the three edges of the unit cell, the positions of the particles are defined by $\vec{r}_i=\theta_1(i)\vec{a}+\theta_2(i)\vec{b}+\theta_3(i)\vec{c}$ where $\theta_1(i)$, $\theta_2(i)$, and $\theta_3(i)$ are all between 0 and 1 and $i=1,2,\ldots,N$. We denote the triad $(\theta_1(i),\theta_2(i),\theta_3(i))$ by $\vec{\theta}(i)$. We start with a fcc lattice and disorder is introduced gradually by heating up the system via a *NPT*-type configurational Monte Carlo simulation where N, P, and T denote the number of particles, pressure, and temperature, respectively. The variables in the simulation are $\vec{a}$, $\vec{b}$, $\vec{c}$, and the $\vec{\theta}$'s for all the particles. After every m (typically two) cycles in the simulation the instantaneous configuraion is used as the initial guess of a conjugate gradient minimization of $(U+P\mathcal{V})$ with respect to all the variables of the simulation. Here U is the potential energy per

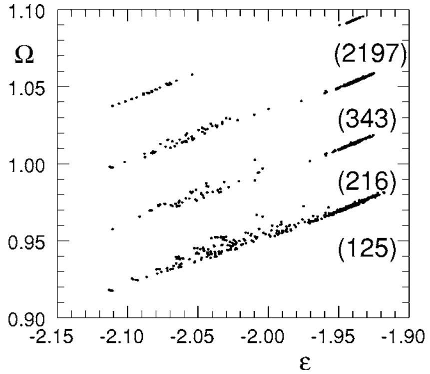

FIG. 1. Volume per particle (Ω) vs energy per particle (ϵ) diagram for LJ potential. To avoid overlap, data for $N=216$, 343, and 2197 are shifted upward with respect to data for $N=125$ by 0.04, 0.08, and 0.12, respectively.

unit cell of volume $\mathcal{V}$ and P is the external pressure (taken to be zero in this paper). This process of generating local minima[21] is repeated with different seeds in the Monte Carlo program. Data for local minima from all the runs are then combined in a volume per particle (Ω) vs potential energy per particle (ϵ) diagram. Figure 1 shows an example of such data for the standard Lennard-Jones (LJ) potential. For each value of N the highest-energy group represents completely amorphous states. This is also confirmed by an inspection of the structure of the pair correlation function. We can pick any local minimum from this group and compute the corresponding harmonic vibrational spectrum.

Let us recall that our goal is to look for shape universality which is said to exist when the plots of the DOS function against frequency for the various systems under consideration can be made to overlap through suitable choices of the scales of frequency and the DOS function. The universality is approximate when the overlap is possible only over a limited part of the spectrum or is poor in quality. When the overlap is excellent over the entire spectrum we call it exact universality. The genesis of our realization of situations in which exact universality can be seen actually lies in a preexisting analysis that attempts to answer the following question: How does increasing disorder cause the transition from the crystalline spectrum with its sharp peaks and van Hove singularities to the amorphous spectrum where such features are missing, and what are the factors that decide the nature of the spectrum in the amorphous region? In this analysis[3] the starting point is a suitable geometry for the solid under consideration. The vibrational spectrum is then considered for the model system obtained by connecting all suitably defined nearest-neighbor pairs with linear springs that have spring constants given by a smooth function of the respective pair distances. Even if this smooth function is actually a positive constant, disorder still removes the sharp features of the crystalline spectrum simply by virtue of altering the connectivity pattern of the springs. Now if the spring constant does vary with pair separation, it will be an extra source of spreading of vibrational time scales and this causes further smearing of the spectrum. It is clear that with large enough disorder and large enough variation of the spring constant, one can expect to have a completely featureless spectrum with a single broad peak in the DOS function. However, the emergence of these characteristics does not automatically imply that the DOS function will display shape universality.

In our approach the relevant configurations are those corresponding to the local minima. Here the pair distances will essentially fluctuate close to the value r_0 that minimizes the pair potential and the simplest dimensionless measure of the dispersion of the spring constant (DSC) for a potential V is given by $\phi \equiv [|\partial^3 V/\partial r^3|_{r=r_0}/|\partial^2 V/\partial r^2|_{r=r_0}]r_0$. Thus a featureless spectrum should be expected when ϕ is sufficiently large. This is precisely what we observe in the examples that follow. More importantly, we find that if an additional but easily realized condition (to be stated later) with a simple geometric meaning is also satisfied during the approach of ϕ to infinity the shape of the spectrum converges to a form that is universal in the sense of being independent of the explicit functional form (representing the potential) whose parameters are varied to change the value of ϕ.

We have investigated two families of potentials for each of which we study the evolution of the amorphous spectrum as a function of the DSC parameter ϕ. The first one, referred to as the generalized Lennard-Jones (GLJ) family, has potentials of the form $V(m,n;r)=(1/r^m-1/r^n)$ with m and n being positive integers ($m>n$). The second one is the Morse family where the potential has only one (positive) parameter α and $V(\alpha;r)=\{\exp[-2\alpha(r-1)]-2\exp[-\alpha(r-1)]\}$. The DSC parameter ϕ is given by $(m+n+3)$ and 3α for the members of the GLJ family and the Morse family, respectively. Common to both the families is the overall shape of the pair potential which always has a single minimum where the potential is negative. At larger distances the potential rapidly rises to zero. At shorter distances also the potential rises rapidly—to a finite value for the Morse case and to infinity for the GLJ case. For the Morse type the rapidity of the rise of the potential away from the minimum is controlled by α, the only parameter present. For the GLJ type, however, the rise of the attractive and the repulsive sides are controlled separately by n and m, respectively, and the limit $\phi\rightarrow\infty$ can be approached either by taking only m or both m and n to infinity. We find that the universal shape of the vibrational spectrum is realized only for the latter route. Thus, stated geometrically, a condition that must always be fulfilled is that the width of the potential well has to keep shrinking from both the repulsive and the attractive sides.

Every local minimum in the amorphous band provides an approximate and finite realization of the amorphous state geometry. This nonuniqueness of the amorphous state geometry is actually a consequence of the fact that the size of the unit cell is finite. When this size is increased progressively, relatively extensive data that we have obtained for the GLJ potential with $m=12$ and $n=6$ (shown in Fig. 1) suggest that the variance of energy per particle, as computed over all the amorphous local minima generated, goes to zero as $1/N$. This type of dependence of the variance on N suggests that the unit cells in the amorphous band can essentially be thought of as random and finite cutouts from the bulk amorphous structure. In view of this the best approximation to the vibrational DOS function for the bulk amorphous state would be to simply take the average of the DOS for all the local minima in the amorphous band for any given value of N. This is the procedure that we have adopted to construct, within our computational formalism, the vibrational DOS function for the bulk amorphous state corresponding to each potential. An estimate of the uncertainty in each data point of the average DOS function is also obtained while combining the data from the various local minima. Once the raw average DOS function is obtained it is straightforward to normalize the average frequency to unity and then to rescale the DOS function $[G(\omega)]$ such that the area under it is also unity. This normalization makes it possible to compare the spectra for different potentials.

Figures 2(a) and 2(b) show how the average DOS function varies with ϕ for sequences of potentials within the GLJ family and the Morse family, respectively. The DOS function seems to be approaching an asymptotic limit within each sequence. To show more clearly this pattern of convergence the insets in Figs. 2(a) and 2(b) also show the DOS function corresponding to the three largest values of ϕ within each sequence. Finally, in Fig. 3 we combine the insets of Figs. 2(a) and 2(b) to compare the convergence patterns of the two sequences. For the GLJ case the data we have presented correspond to a sequence in which $m=n+2$. We have also investigated the sequence in which $m=n+4$ with $n=4,6,8,10,12,14,16$, and 18. Results for this latter sequence also lead to the same conclusions as those with the $m=n+2$ sequence and are not reported here. Data of the type presented in Figs. 2 and 3 form the basis of our inference that not only do the DOS functions show convergence within each sequence but also they converge to an asymptotic function that is independent of the family that the sequence of potentials is drawn from. It is thus plausible to form a more general conjecture that for a broad class of parametric functional forms of the pair potential there is a universal form of the DOS function over the entire spectrum in the limit of large dispersion of the spring constant—provided the sharpness of the rise of the potential away from the minimum increases without limit for both the attractive and the repulsive sides of the minimum. A possible explanation of the universality over large parts of the spectrum that has been reported recently[15–17] then emerges. This has to do with (1) the existence of exact asymptotic universality and (2) the fact that the dependence of the spectrum on the potential function becomes rather weak well before asymptotic conditions are reached [see Figs. 2(a) and 2(b)]. Thus many realistic potentials will satisfy the conditions of approximate universality. However, it is also equally clear that the spectra can be far from universal in some situations (e.g., for smaller values of ϕ). It is only a question of how far the relevant potential is from the asymptotic conditions of exact universality. Finally, to compare the universal DOS function that we obtain with experimental data we show, in the inset of Fig. 3, $G(\omega)/\omega^2$ against ω in a semilogarithmic plot. There is indeed an extended linear section in the middle—as is the case with the data for molecular glasses presented in Figs. 3(b), 3(c), and 3(d) in Ref. 15.

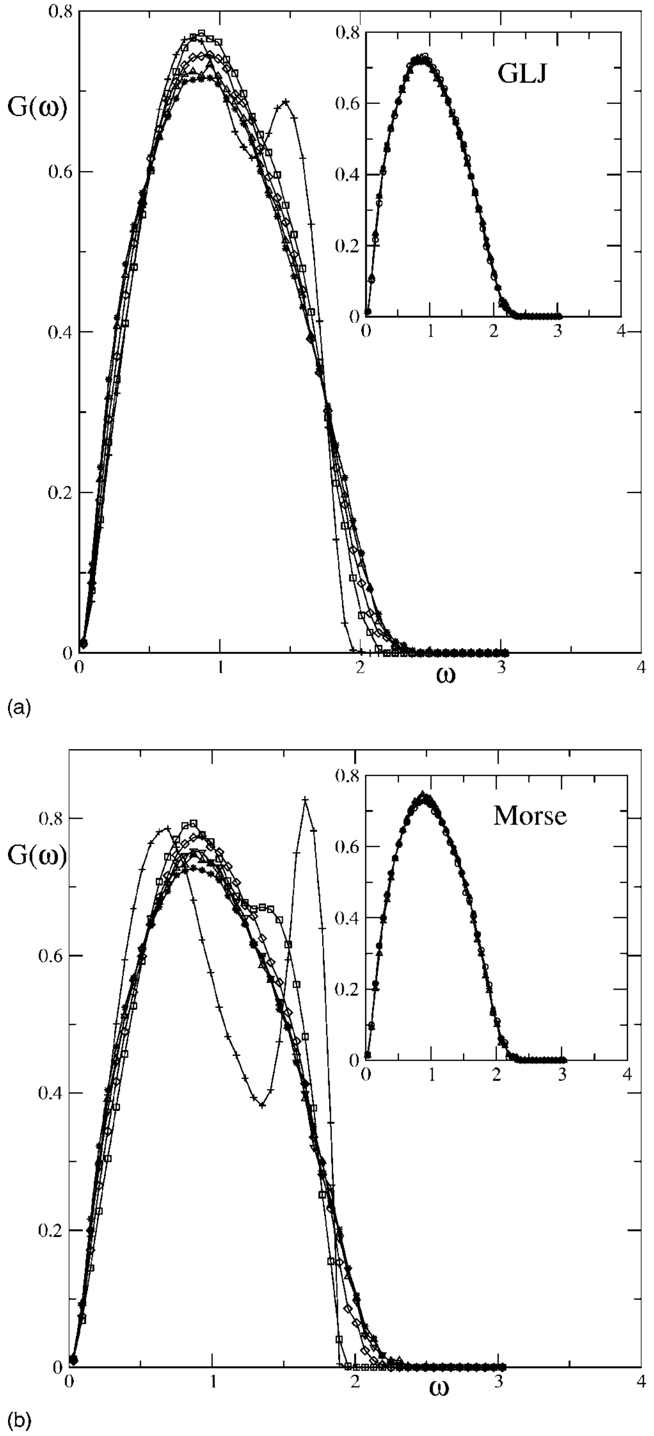

FIG. 2. Normalized density of states $[G(\omega)]$ vs normalized frequency (ω) in the fully disordered region for some selected cases. (a) GLJ potential: The values of $[m,n]$ are [6,4] (cross), [10,8] (square), [14,12] (diamond), [18,16] (triangle), and [22,20] (star). Inset: [22,20] (star), [20,18] (triangle), and [18,16] (circle). (b) Morse potential: The values of α are 3.0 (cross), 4.5 (square), 7.5 (diamond), 10.5 (inverted triangle), 13.5 (triangle), and 16.5 (star). Inset: 16.5 (star), 15.0 (circle), and 13.5 (triangle).

We now address the issue of understanding the origin of the apparent universality. We recall that the vibrational spectrum is obtained by diagonalizing the dynamical matrix which depends on (a) the statistical aspects of the distribution of particles in the unit cell and (b) how the second derivative of the pair potential varies with pair separation. Thus the starting point of an explanation of the asymptotic univer-

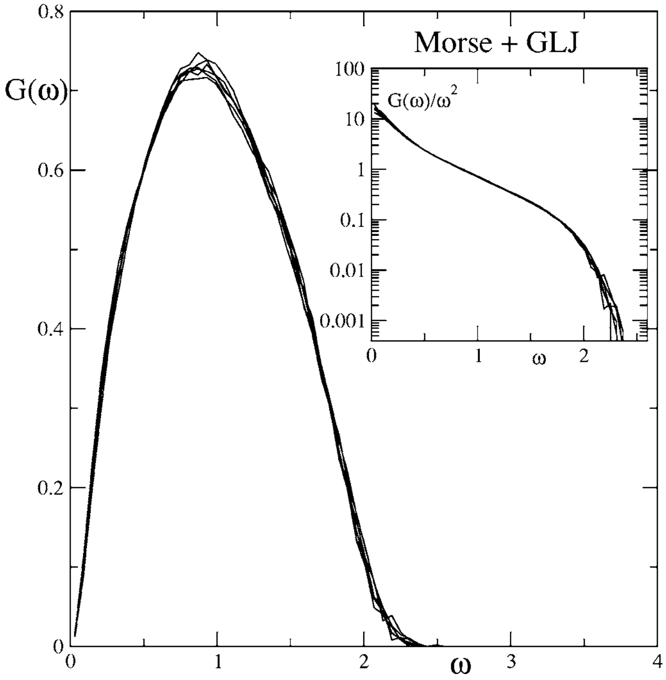

FIG. 3. Superposition of the insets of Figs. 2(a) and 2(b) to compare the convergence patterns of the GLJ and the Morse families. Inset: Data on $G(\omega)$ shown in the main figure are divided by ω^2 and shown in a semilogarthmic plot for the purpose of comparison with experimental data.

sality would be a study of the evolution of the amorphous structure as the pair potential shrinks in width within each family. Consideration of the energy of the system would suggest that for a potential with a narrow well and a strong repulsive core the width of the first peak in the pair correlation function would be correspondingly small and should keep decreasing as the width of the potential well decreases. Thus, for all pairs of particles with nonvanishing interaction, the pair distance should be very close to the value r_0 that minimizes the pair potential. This expectation is indeed confirmed by the data in Table I in which we present, for both the GLJ and the Morse families, the data regarding this distance (r_0). This table also contains data on the location and the full width at half maximum of the first peak of the pair correlation function. Here we have denoted the distance corresponding to the maximum of the first peak by r_p, and the distances for the two half-maximum points by r_+ ($>r_p$) and r_- ($<r_p$). Thus a measure quantifying the pattern of shrinkage of the first peak would be the ratio $\chi=(r_+-r_-)/r_p$. Values of this parameter are also available in Table I and it can be seen that the distribution of the nearest-neighbor pair distances becomes progressively narrower when the well of the pair potential shrinks. Let us remember that for a sufficiently narrow potential well only the nearest-neighbor pairs make nonvanishing contribution to the dynamical matrix. However, while the distribution of these nearest-neighbor distances becomes very narrow, the actual contributions to the dynamical matrix are still distributed over a rather wide range. This is a consequence of the fact that the dynamical matrix involves the second derivatives of the potential and also that we are dealing with the limit of the dispersion of the spring constant (ϕ) going to infinity. Thus a shrinkage of the range of nearest-neighbor distances may not result in a shrinkage of the range of second-derivative values corresponding to these nearest-neighbor distances. As a normalized measure of the range of variation of the second-derivative values appearing in the dynamical matrix we can define a parameter $\beta=[V''(r_-)-V''(r_+)]/V''(r_p)$. If, in the limit of ϕ going to infinity, β went to zero and the statistical geometry of the configurational disorder also displayed convergence in some suitable sense, it would have constituted a relatively simple scenario compatible with the shape universality of the vibrational spectrum. However, this scenario is not supported by the data on β that are given in Table I. The value of β stays at the level of unity rather than converging to zero. Thus, the real reason behind universality has to be more subtle than what is suggested by the simple scenario mentioned above.

III. DISCUSSION AND CONCLUSION

The central point of this paper is the following proposition: Underlying the quasiuniversality in the shape of vibra-

TABLE I. Geometrical aspects of the first peak of the pair correlation function: variation with potential.

Potential	Parameter α or $[m,n]$	r_-	r_p	r_0	r_+	χ	β
Morse	4.5	0.884	0.919	1.0	0.975	0.099	0.964
	7.5	0.956	0.981	1.0	1.018	0.063	1.212
	10.5	0.974	0.991	1.0	1.016	0.042	1.181
	13.5	0.982	0.995	1.0	1.014	0.032	1.176
	16.5	0.986	0.996	1.0	1.011	0.025	1.118
GLJ	$[8,6]$	1.033	1.068	1.155	1.124	0.085	1.092
	$[10,8]$	1.050	1.079	1.118	1.125	0.070	1.186
	$[14,12]$	1.046	1.067	1.080	1.097	0.048	1.255
	$[18,16]$	1.039	1.054	1.061	1.076	0.035	1.148
	$[22,20]$	1.033	1.045	1.049	1.060	0.026	1.086

tional spectra that has been observed in some recent experimental and computational studies of amorphous systems there is an exact universality over the entire spectrum that can be realized in appropriate limiting situations. We have presented numerical data for two families of potentials in support of this possibility. The forms of the potentials used here are suggested by the fact that exponentials and power laws are the elementary functions most suited for describing the rapidly varying (with distance) nature of interatomic or intermolecular forces. It would obviously be desirable to study other physically meaningful combinations of these or other functions to see how generally applicable are our inferences.

Also since our central hypothesis is based on the assumption of asymptotic convergence of the normalized DOS curves it is important to make a critical assessment of the quality of the evidence on which it is based. For example, let us consider the insets of Figs. 2(a) and 2(b) where we have shown the spectra for the three narrowest potentials for the GLJ case and the Morse case, respectively. Closer examination of these two figures shows that, while the quality of convergence is excellent in the high-frequency domain, there is actually some deviation from convergent behavior in the low-frequency segment below the peak of the DOS function. In the present context deviation from convergent behavior means that the relative shift between any pair of curves (out of the three in either inset) is systematic and is beyond the range permitted by our estimate of the uncertainty in the DOS data. Of course it may simply mean that we are not yet close enough to the asymptotic limit. But it remains a moot point for us since there are serious practical difficulties associated with computations using even narrower potentials. One problem is that even when the number (N) of particles in the unit cell is rather small, as in our case, convergence of the geometry becomes very slow while computing the local minima for potentials with such narrow wells. Choice of the value of N is another important issue. Testing how close we are to the bulk limit necessarily requires checking the convergence with respect to this number as it keeps increasing. However, as N is increased, the requirement of computational resources goes up very rapidly—more so when the potential has a narrower well. In principle, it is certainly possible to test whether the slight lack of convergence in our low-frequency data is due to the practical problems mentioned above or is a reflection of a genuine absence of exact universality. In either case, however, the validity of the comparison of our data with the experimental results for glassy systems is unlikely to be affected, i.e., there is a very large range of potentials for which the vibrational DOS in the amorphous state is rather weakly dependent on the potential and displays quasiuniversal features. In our opinion this itself is rather remarkable—independent of what the true picture turns out to be in the asymptotic limit.

Finally, assuming the validity of our conjecture of universality, the question of its origin arises naturally. As we have discussed earlier the answer is not known presently. But it is our belief that the asymptotic nature of the interaction potential will prove to be the facilitating factor in calculating the spectrum analytically and thus demonstrating its universality.

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