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Single-random-valley approximation in vibration-transit theory of liquid dynamics

Giulia De Lorenzi-Venneri and Duane C. Wallace
Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA

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The first goal of vibration-transit theory is to be able to calculate from a tractable partition function and without adjustable parameters the thermodynamic properties of the elemental monatomic liquids. The key hypothesis is that the random class of potential energy valleys dominates the statistical mechanics of the liquid at temperatures above melting $T \gtrsim T_m$ and that these valleys are macroscopically uniform in the thermodynamic limit. This allows us to use a single random valley to calculate the vibrational contribution to liquid properties, exactly in the thermodynamic limit, and as an approximation at finite number of particles N. This approximation is tested here for liquid Na with a physically realistic potential based on electronic structure theory. Steepest descent quenches were made from the molecular dynamics equilibrium liquid ($N=500$) at temperatures from $0.90T_m$ to $3.31T_m$, and six potential parameters were calculated for each structure, namely, the potential energy and five principal moments of the vibrational frequency distribution. The results show temperature-independent means and small standard deviations for all potential parameters, consistent with random valley uniformity at $N \to \infty$, and with finite-N broadening at $N=500$. The expected error in the single random valley approximation for Na at $N=500$ and $T \gtrsim T_m$ is 0.1% for the entropy and 0.5% for the internal energy, negligible in the current development of liquid dynamics theory. In related quench studies of recent years, the common finding of nearly temperature-independent means of structural potential energy properties at $T \gtrsim T_m$ suggests that the single random valley approximation might also apply to systems more complicated than the elemental liquids.

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I. INTRODUCTION

To place the present work in the context of current physics research, it is helpful to outline some relevant theoretical development. Pseudopotential perturbation theory was developed as a model electronic structure theory for nearly free electron metals. The basic concept was well described by Sham [1] in his calculation of the phonon spectrum of Na, and by Harrison [2] in his formulation of the total adiabatic potential [the form of that potential is written here in Eq. (4)]. Successful calculations were made of the compressibilities and binding energies of simple metals [3], and of temperature-dependent thermodynamic properties [4]. As a matter of principle the theory applies as well to the liquid as to the crystal. A study was made of the resistivities of the elemental liquids [5]. Reviews were made of the application of pseudopotential perturbation theory to liquid metals [6,7], and comparisons of theory and experiment were also reviewed [8]. As a result of these studies and many more, it is clear by now that pseudopotential perturbation theory can provide realistic interatomic potentials for the simple metals and alloys. The same theory is also applicable to a broad range of problems, as illustrated by a recent application to electron phonon interactions [9,10].

Classical molecular dynamics (MD) has been developed to calculate statistical mechanical averages over the atomic motion for many-atom systems. Results are obtained for real materials when realistic interatomic potentials are used, and these are commonly based on pseudopotential perturbation theory for the nearly free-electron metals. MD calculations have been used to assess the validity of anharmonic theory in the dynamic structure factor $S(q,\omega)$ of bcc K [11] and to evaluate the temperature dependence of the elastic constants of bcc Na [12]. MD has a larger role to play in liquids than in crystals, since the entire atomic motion is *a priori* unknown in liquids. Good agreement with experiment was obtained for $S(q,\omega)$ in liquid Rb [13], for thermodynamic properties of liquid Na [14], the static structure factor of liquid Li [15] and of the remaining alkali metals [16], and shear viscosity of Rb [17,18]. MD calculations are considered sufficiently accurate to substitute for experimental data, in order to assess the validity of theory in cases where laboratory experiments are not available. Calculations carried out from this point of view include transverse current correlation functions for alkali metals [19,20], Brillouin peak dispersion curves for alkali metals [16,20], the shear stress autocorrelation function for Rb [21], and transport coefficients for Lennard-Jones (LJ) Ar [22]. By now it is clear that, from the correct interatomic potentials, MD can give accurate results for equilibrium and nonequilibrium properties of condensed matter phases.

Here we are interested in the atomic motion and statistical mechanics based on this motion for the monatomic elemental liquids. The most well developed theory for equilibrium thermodynamic properties is based on the interatomic pair potential and the pair distribution function [7,23]. Nonequilibrium theories are currently much less developed. For the dynamic structure factor, simplifying approximations for the glassy state are discussed by Egelstaff [24], and a Feynman-like collective mode approximation is applied to classical elemental liquids by March and Alonso [25]. The formally exact memory function analysis for $S(q,\omega)$ described, for example, by Hansen and McDonald [26], or by Balucani and Zoppi [27], can be parametrized and fitted to experimental data for liquid metals [28]. Empirical relations for the shear viscosity of the elemental liquids are compared with experiments by March and Tosi [29] and by Chisolm and Wallace [30].

In vibration-transit (VT) theory our aim is to develop a different and complementary path in the study of liquid dynamics: a formulation based on an approximate but tractable zeroth order Hamiltonian, from which both equilibrium and nonequilibrium properties can be calculated for the elemental liquids without adjustable parameters. From this point we hope to systematically improve our understanding of the atomic motion by studying the corrections beyond the zeroth order formulation.

The idea of quenching a MD system from the equilibrium liquid, to find and examine the inherent structures which underlie the atomic motion, was pioneered by Stillinger and Weber [31–33]. This quickly became an indispensable technique for studying the potential energy landscape, and for seeking relations between this landscape and the dynamic properties of the system [34–36]. Progress in this area is described in the monographs of Binder and Kob [37], of Wales [38], and in the review of Sciortino [39]. In the area of thermodynamic properties, application was made to the equation of state of soft spheres [40], and of models for water [41] and orthoterphenyl [42].

The key approximation in VT theory is that the random class of many-atom potential energy valleys dominates the potential surface and that these valleys all have the same structural potential and distribution of vibrational mode frequencies [43]. Hence a single random valley suffices to calculate vibrational properties of the liquid state. In equilibrium statistical mechanics, the primary role of transits is to allow the system to access the multitude of random valleys, and thus to possess the corresponding liquid configurational entropy. This formulation already gives a good account of the thermodynamic properties of the elemental monatomic liquids at melt [43]. In nonequilibrium statistical mechanics the vibrational contribution plus a transit model gives a respectable account of the velocity autocorrelation function for liquid Na [44]. Moreover the *a priori* vibrational contribution accounts for the measured Brillouin peak dispersion curve of liquid Na within experimental error [45], and with an added model for transits gives a good description of the entire dynamic structure factor [46].

At this point in the theoretical development it is important to make a quantitative study of the key "single random valley" approximation in VT theory. In earlier work [47,48], means and standard deviations were listed for potential parameters for 10 random structures with mixed N (500 or 1000). Since the number of samples was so small, and since the standard deviations vary with N, those results are not useful for a quantitative estimate of errors. Here, by doing more quenches at fixed N (500), we make statistically meaningful estimates of the errors involved in the single random valley approximation when VT theory is compared with experiment for thermodynamic properties. These estimates are important for assessing the accuracy of the basic theory. Also in the earlier work, the ten random structures examined were all quenched from the same initial liquid temperature of 395 K. Since then, glass transition studies have found a Gaussian distribution of structural potentials in binary Lennard-Jones systems [49–51], a distribution which gives a strong dependence of the mean structural potential on the temperature from which the system is quenched. While we are studying the liquid state and not the glass transition, the effect of such a distribution remains present, in principle, at any finite temperature. This would require a modification of the single random valley approximation. We therefore need to quench from a wide range of temperatures in order to rule out, or account for, a dependence of the structural potential properties on the temperature from which the system is quenched.

The single random valley approximation will be described in Sec. II, to clarify the questions to be investigated. In Sec. III, our methods are presented and results are discussed. Section IV compares our results with related quench studies, including those which observe the Gaussian distribution, and conclusions are briefly listed in Sec. V.

II. THE SINGLE RANDOM VALLEY APPROXIMATION

The many-atom potential surface consists of a very large number of intersecting nearly harmonic potential valleys, each of configurational dimension $3N$ for an N atom system. For a given valley the structural potential (the total system potential at the valley minimum) is Φ_0, the normal vibrational frequencies are ω_λ, $\lambda=1,\ldots,3N-3$, and the characteristic temperature θ_0 is given by

$$\ln k\theta_0 = \frac{1}{3N-3}\sum_\lambda \ln \hbar\omega_\lambda. \tag{1}$$

The valleys are labeled with superscript γ, and their most important potential properties are Φ_0^γ and θ_0^γ. The extended valley is defined for each valley as its harmonic extension to infinity. Then if we neglect the anharmonicity of each valley, and neglect also the presence of valley-valley intersections, the classical partition function arises from harmonic vibrational motion in each of the extended valleys

$$\mathcal{Z}_N = \sum_\gamma e^{-\beta\Phi_0^\gamma}(T/\theta_0^\gamma)^{3N}. \tag{2}$$

This is then subject to corrections for anharmonicity and intervalley intersections.

Many-atom potential valleys have long been classified as crystalline and amorphous. The separation of amorphous valleys into symmetric and random classes [43] was motivated by experimental data for the normal melting [52] elements. First, the atomic motional specific heat for both liquid and crystal is close to $3k$ per atom, and suggests nearly harmonic vibrations in the liquid, as is certainly the case for the crystal. The result further indicates a rather constant value of Φ_0 among the contributing valleys for each element, because a significant distribution of Φ_0 would appear in the specific heat. Second, the entropy of melting at constant volume is a rather universal constant [53], suggesting the universal number w^N of contributing valleys for the elements, where $\ln w = 0.80$ [43,54]. This result also indicates a rather constant value of θ_0 among the contributing valleys for each element, because a significant distribution of θ_0 would appear in the entropy of melting. However, for a given element, we know there are many symmetric valleys in the potential surface, for example those with polycrystal and microcrystal structures, and that these valleys have as a result of their various symmetries a wide variation in Φ_0 and θ_0 values. The logical indication is that there also exist random valleys, with minimal orientational and translational order, and that the randomness itself provides for both numerical superiority and uniform potential properties of these valleys. If we therefore neglect the symmetric valleys, and take the random valleys to number w^N, and for each element to have all the same structural potential Φ_0^l and characteristic temperature θ_0^l, the partition function Eq. (2) simplifies to

$$\mathcal{Z}_N^l = w^N e^{-\beta\Phi_0^l}(T/\theta_0^l)^{3N}. \tag{3}$$

The superscript l refers to the liquid, and indicates any one of the many equivalent extended random valleys. Equation (3) is still subject to the corrections applying to Eq. (2), for anharmonicity and intervalley intersections.

The preceding arguments from experimental data are clearly qualitative. They are sufficient to justify the single random valley approximation, as expressed in Eq. (3), as a zeroth order approximation, but they are of little help in evaluating the accuracy of this approximation. By far the most precise way to make this evaluation for a real material is from MD calculations with a physically realistic potential. The theoretical background outlined in the Introduction is crucial to this program.

III. METHODS AND RESULTS

We work with an interatomic potential which accurately represents metallic Na at the density of the liquid at melt at zero pressure. For N atoms in a volume V, the positions of the nuclei are $\boldsymbol{r}_K$, $K=1,\ldots,N$, and the total system potential $\Phi(\{\boldsymbol{r}_K\})$ is [2]

$$\Phi(\{\boldsymbol{r}_K\}) = \Omega(V) + \frac{1}{2}\sum_{K,L}\phi(|\boldsymbol{r}_K-\boldsymbol{r}_L|;V). \tag{4}$$

$\Omega(V)$ is a large negative potential which accounts for most of the metallic binding, and $\phi(r;V)$ is the effective internuclear potential. Since V is fixed, $\Omega(V)$ is constant, and the zero of energy is chosen by setting $\Omega(V)=0$. The MD system has $N=500$ atoms in a cubical volume, with periodic boundary conditions; further information on the potential and the MD system may be found in Ref. [47].

For each structure, Φ_0 was evaluated, as well as the complete set $\{\omega_\lambda\}$ of vibrational frequencies. Instead of the frequency distribution, we report the physically important characteristic temperatures θ_n for $n=-2,-1,0,1,2$. The spectrum average of a function $f(\omega_\lambda)$ is most accurately calculated directly from the frequencies, as

$$\langle f(\omega_\lambda)\rangle = \frac{1}{3N-3}\sum_\lambda f(\omega_\lambda). \tag{5}$$

θ_0 is given by Eq. (1), and is related to the log moment of the frequency distribution, while θ_n for $n=-2,-1,1,2,\ldots,$ is given by

$$k\theta_n = \left[\frac{n+3}{3}\langle(\hbar\omega_\lambda)^n\rangle\right]^{1/n}. \tag{6}$$

For any harmonic vibrational system, $\frac{9}{8}Nk\theta_1$ is the quantum zero-point energy, θ_{-2} is related to the classical mean square displacement, and θ_2 gives the leading quantum correction to the free energy at high temperatures (Ref. [54], Secs. 16, 17, and 23).

The melting temperature for Na at 1 bar is 371 K, and quenches were made from the equilibrium liquid at temperatures from 0.90 to $3.31T_m$. The reason for varying the temperature is to reveal the distribution of Φ_0 and θ_0 among the valleys accessible to the liquid. To illustrate, let us write the partition function Eq. (2) as an integral

$$\mathcal{Z}_N = \int\int G(\Phi_0,\theta_0)e^{-\beta\Phi_0}(T/\theta_0)^{3N}d\Phi_0 d\theta_0, \tag{7}$$

where $G(\Phi_0,\theta_0)$ is the correlated distribution of Φ_0 and θ_0 over valleys. Then the average of Φ_0 observed at temperature T is

$$\langle\Phi_0\rangle = \frac{\int\int \Phi_0 G(\Phi_0,\theta_0)e^{-\beta\Phi_0}(T/\theta_0)^{3N}d\Phi_0 d\theta_0}{\mathcal{Z}_N} \tag{8}$$

with a similar equation for $\langle\theta_0\rangle$. The observed temperature variations of $\langle\Phi_0\rangle$ and $\langle\theta_0\rangle$ will reveal the variations of $G(\Phi_0,\theta_0)$. From Eq. (7), as temperature is lowered, both $\langle\Phi_0\rangle$ and $\langle\theta_0\rangle$ move to lower values within the distribution $G(\Phi_0,\theta_0)$. The only distribution giving a temperature-independent $\langle\Phi_0\rangle$ or $\langle\theta_0\rangle$, is a δ function on Φ_0, or a δ function on θ_0, respectively.

We quenched by steepest descent, iterating $\Delta\boldsymbol{r}_K=\boldsymbol{f}_K(\Delta t)^2$, where $\boldsymbol{f}_K$ is the force on atom K and the atomic mass is absorbed in $(\Delta t)^2$. While the total potential is monotonically decreasing, other potential energy functions are not. The lowest eigenvalues $(M\omega_\lambda^2)$ are negative at first, and they increase, but not smoothly. Eventually all the eigenvalues become positive and the final convergence proceeds. Of the characteristic temperatures θ_n, the last to converge is θ_{-2}. The convergence criterion is set at $\Delta|\Phi/N| = 10^{-20}$ mRy/atom. For comparison, $kT_m=2.3$ mRy for Na.

Our results for 30 quenches at each temperature are listed in Table I. Since the potential contribution $\Omega(V)$ is omitted [see Eq. (4)], the Φ_0 data are missing most of the binding energy, about 80 mRy/atom, but this is of no consequence since we are concerned only with potential energy differences. Note that θ_{-2} is a measure of $\langle\omega_\lambda^{-2}\rangle$, which depends strongly on the few lowest frequencies, and this gives rise to the large standard deviations for θ_{-2}. The same effect is present but much weaker in θ_{-1}. The data of Table I are in agreement with previous averages for a small collection of random valleys [47]; differences are likely due to averaging together different values of N in the earlier work.

The key property of the random valley data in Table I is their temperature independence, and the implied narrowness of the underlying distribution. For each potential parameter, Φ_0/N and each θ_n, all means lie well within the standard

TABLE I. Results from 30 steepest descent quenches from the liquid at five temperatures. Under number of structures, (r) indicates random and (s) symmetric. Potential parameters are listed as mean ± standard deviation for the random sets, and are listed individually for the two symmetrics.

T (K)	T/T_m	Number	Φ_0/N (mRy/atom)	θ_{-2} (K)	θ_{-1} (K)	θ_0 (K)	θ_1 (K)	θ_2 (K)
335	0.90	30(r)	-13.478 ± 0.034	112 ± 5	125.1 ± 1.0	98.60 ± 0.20	147.04 ± 0.08	154.09 ± 0.10
399	1.08	30(r)	-13.478 ± 0.041	113 ± 3	125.3 ± 0.9	98.64 ± 0.21	147.07 ± 0.08	154.11 ± 0.11
625	1.68	29(r)	-13.461 ± 0.038	112 ± 4	124.9 ± 1.0	98.53 ± 0.22	147.02 ± 0.08	154.13 ± 0.10
799	2.15	30(r)	-13.472 ± 0.028	113 ± 3	125.4 ± 0.7	98.62 ± 0.15	147.04 ± 0.06	154.09 ± 0.08
1228	3.31	29(r)	-13.485 ± 0.041	114 ± 2	125.6 ± 0.8	98.71 ± 0.21	147.09 ± 0.08	154.09 ± 0.12
all		148(r)	-13.475 ± 0.037	113 ± 4	125.3 ± 0.9	98.62 ± 0.20	147.05 ± 0.08	154.10 ± 0.10
625	1.68	1(s)	-14.25	134	137	102.2	147.8	152.2
1128	3.31	1(s)	-13.94	125	132	100.5	147.4	152.9

deviation of every set. This property is illustrated in Fig. 1 for Φ_0/N. Hence there is no significant temperature dependence of the means, and each distribution can be considered a δ function broadened by finite-N effects.

In the single random valley approximation, in order to compare theory with experimental data for a real liquid, we want the potential parameters of the representative random valley in the thermodynamic limit. The best finite-N estimate we have for the parameters is their mean values as listed in Table I. If then a single random valley is chosen for statistical mechanics calculations, the expected errors of its parameters are given by the standard deviations in Table I. For the thermodynamic properties of liquid Na at $T \gtrsim T_m$ and at $N = 500$, the error is expected to be within the following limits: (a) 0.1% for the entropy S at T_m and decreasing as T increases from the standard deviation of θ_0 for random valleys and (b) 0.5% in the internal energy U at T_m and decreasing as T increases from the standard deviation of Φ_0/N for random valleys (U is measured relative to the energy of the crystal at $T=0$ and $P=0$). These errors are of the same magnitude as experimental errors in the thermodynamic data for liquid Na at T_m, and are currently negligible in the development of a highly accurate liquid dynamics theory.

Of our 150 quenches, the system arrived at a symmetric structure in two cases. This happens when the system at low potential energy finds a way through many quench iterations to organize a region of spatial symmetry. The process is apparently facilitated by the periodic boundary condition and is therefore a finite-N effect. This conclusion is supported by our earlier results using the same quench procedure [47], where the liquid Na system at 400 K invariably quenched to a symmetric structure at $N=168$, but was not observed to do so at $N \gtrsim 500$. Also, while as far as we are aware LJ systems do not usually quench to symmetric structures, several crystallinelike structures were observed at $N=29$ by Angelani *et al.* [55]. It is likely that the soft repulsive core of the Na potential makes it easier to wiggle into a symmetric structure than it is for the LJ potential. Individual data for our symmetric structures are listed in Table I, where it is seen that the potential parameters are many standard deviations away from the random distribution.

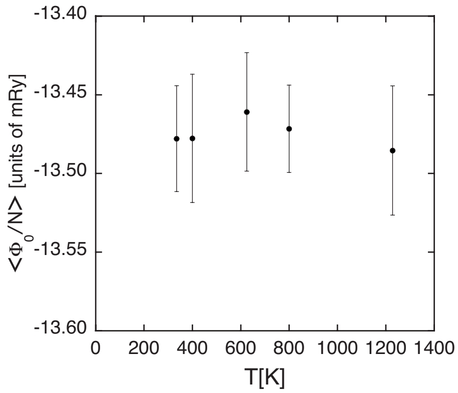

FIG. 1. Potential energy of quenched structures Φ_0/N in mRy as a function of the temperature of the initial configurations.

IV. COMPARISON WITH RELATED QUENCH STUDIES

From a detailed study of binary LJ systems, Heuer and Büchner [49] were able to determine the underlying distribution of inherent structure energies (our Φ_0). The quantity they evaluated is $G_{\text{eff}}(\Phi_0)$, which in our notation is [see Eq. (7)]

$$G_{\text{eff}}(\Phi_0) = \int G(\Phi_0,\theta_0)(T/\theta_0)^{3N} d\theta_0. \tag{9}$$

They showed $G_{\text{eff}}(\Phi_0)$ is temperature independent at low temperatures $kT \lesssim 1$ and is accurately Gaussian in the center, with a possible small non-Gaussian contribution in the wings. Since LJ systems that crystallize have $kT_m \sim 1$, we consider this value as a surrogate kT_m for binary systems also, for the purpose of scaling system properties with melting temperature. An important property of the Gaussian distribution, provided it has the correct N dependence [50], is that it gives a contribution to the free energy which remains as $N \to \infty$, and in which both the Gaussian mean and variance appear. This contribution becomes increasingly important as T decreases toward the glass transition. For an underlying Gaussian $G_{\text{eff}}(\Phi_0)$, the function $G_{\text{eff}}(\Phi_0)e^{-\beta\Phi_0}$ is a Gaussian with constant width whose mean Φ_0 shifts downward as T^{-1}. This property is clearly shown by the quench results of Sciortino, Kob, and Tartaglia for binary LJ systems [Fig. 1(a) of Ref. [34] and Fig. 4 of Ref. [51]].

Because $\langle \Phi_0 \rangle$ shows no meaningful temperature dependence in Fig. 1, our quench data show no evidence of a Gaussian distribution of Φ_0, for liquid Na at $T \gtrsim T_m$. Interestingly, the same property is exhibited by the binary LJ system mentioned above, since the temperature-dependent Gaussian $G_{\text{eff}}(\Phi_0)e^{-\beta\Phi_0}$ does not shift with temperature at $kT \gtrsim 1$ [34,51]. Indeed, MD calculations commonly show very little temperature dependence for the mean inherent structure energy at $kT \gtrsim 1$. Examples for binary LJ systems are shown in Fig. 1(a) of Ref. [56], Fig. 1(a) of Ref. [57], Fig. 2 of Ref. [58], Fig. 5 of Ref. [59], and Fig. 2(A) (lower) of Ref. [60]. The same result for a monatomic LJ system is shown in Fig. 2 of Ref. [61], and for a model of water in Fig. 1(b) of Ref. [62]. In addition, the vibrational mode distribution $g(\omega)$ and/or the average $\langle \ln \hbar\omega \rangle$ is evaluated in several of these studies, and these quantities also show very little temperature dependence at $kT \gtrsim 1$; see, e.g., Figs. 6 and 7 of Ref. [60], Figs. 2(a) and 3 of Ref. [57], and Figs. 1(b) and 2(c) of Ref. [62]. All these results are consistent with a class of valleys with highly uniform potential energy properties, which are statistically dominant at $kT \gtrsim kT_m$, as we find in Na.

In this connection, we suppose that the quench technique itself does not affect the statistical average results of our study or the other studies mentioned. This view is supported by the demonstration of Chakravarty *et al.* [63], that two variations of the conjugate gradient quench procedure lead to the same average structural properties for a LJ system.

V. CONCLUSIONS

In the early development of VT theory, the hypothesis was made concerning the potential energy surface which underlies the motion of monatomic liquids [43]: (a) the random valleys are of overwhelming numerical superiority and hence dominate the statistical mechanics at $T \gtrsim T_m$ and (b) the random valleys all have the same macroscopic potential properties, e.g., the structural potential and the vibrational frequency distribution, in the thermodynamic limit. The present results are consistent with this hypothesis for the example of liquid Na, with the observed spread of random valley potential parameters and the occasional appearance of a symmetric structure attributed to finite-N effects.

This hypothesis allows us to express the vibrational contribution to a thermodynamic function or to a time correlation function in terms of a single random valley in the thermodynamic limit. When one chooses a single random valley for practical calculations, at finite N, an error is present because of the spread of random valley potential properties at finite N. For liquid Na at $N=500$ and $T \gtrsim T_m$, the corresponding expected error in the entropy and the internal energy is of the same order as experimental error in these quantities, and hence is negligible in the current development of an accurate liquid dynamics theory.

Compared to the present results, more accurate data can be obtained by increasing N. The two important trends with increasing N are, at constant T: (a) each mean value approaches its thermodynamic limit, presumably going as N^{-1} when periodic boundary conditions apply and (b) the standard deviations are expected to approach zero, possibly as $N^{-1/2}$. Hence increasing N will provide more accurate random valley parameters, for comparison of theory with experiment, and will also provide a more accurate test of the single random valley approximation.

In comparing the present results with related quench studies, we observe that nearly temperature-independent mean values at $T \gtrsim T_m$ have been reported for the inherent structure energies (our Φ_0) and for the log moment of the vibrational frequency distribution (our θ_0) for binary LJ systems [56–60], for a monatomic LJ system [61], and for a model of water [62]. This suggests that our hypothesis for monatomic liquids, of a class of numerically dominant and macroscopically uniform potential energy valleys, might apply to these systems also.

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