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Exponential multiplicity of inherent structures

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The mechanically stable spatial arrangements of interacting molecules (potential energy minima, ''inherent structures'') provide a discrete fiducial basis for understanding condensed phase properties. Simple plausibility arguments have been advanced previously suggesting that at fixed positive density the number of distinguishable inherent structures rises exponentially with system size. A more systematic analysis is presented here, using lower and upper bounds, that leads to the same conclusion. Further examination reveals that the characteristic exponential rise rate for inherent structure enumeration diverges as the density approaches zero, when attractive interparticle forces are present. [S1063-651X(99)07001-4]

I. INTRODUCTION

One of the intrinsic difficulties faced by the field of nonlinear optimization is that many problems of interest present large numbers of ''false'' solutions. In the case of an objective function requiring minimization, the global absolute minimum may be hidden as a needle in a proverbial haystack of local nonabsolute minima, possibly requiring an exhaustive search and comparison procedure. Indeed, many families of problems are known for which the total number of minima rises at least exponentially as the number of variables increases [1].

Under some circumstances it may be valuable to identify and classify the entire collection of minima from the ''best'' to the ''worst,'' i.e., from the absolute minimum to the highest-lying local minimum. This is the case in condensed matter physics/materials science where the objective function in one important application is the potential energy of interaction Φ for the constituent particles and its minima represent the mechanically stable arrangements of those particles in space (''inherent structures'') [2,3]. If the particles involved number N and are structureless, Φ would have to be minimized over the $3N$-dimensional space of particle positions $\mathbf{r}_1,\ldots,\mathbf{r}_N$. If each particle additionally possessed ν internal degrees of freedom (describing orientation, vibrational amplitudes, or conformation), the relevant configurational space over which Φ would have to be minimized would have dimension $(3+\nu)N$.

Let $\Omega(N,V)$ be the number of Φ minima when N particles are confined to a volume V of given shape. For a single-component system (all particles identical) it is useful to write

$$\Omega(N,V) = N!\,\Omega_1(N,V). \tag{1.1}$$

This accounts for the fact that with hard walls present each minimum is but one of $N!$ equivalent minima that differ only by permutation of identical particles. [When periodic boundary conditions are imposed on V, the resulting free transla-

tion requires that the $N!$ factor in Eq. (1.1) be replaced by $(N-1)!$.] Consequently Ω_1 only enumerates geometrically distinct minima.

It has been argued [2,3] for realistic model potentials Φ that Ω_1 asymptotically rises exponentially with system size N (with $N/V>0$ held fixed and the shape of V held fixed). More precisely, the claim has been that

$$\lim_{N\to\infty} (N^{-1}\ln \Omega_1) = \alpha, \quad \alpha > 0. \tag{1.2}$$

The exponential rise rate parameter α is expected to be substance specific and to depend on the number density N/V. The tentative validity of relation (1.2) rests partly on the fact that some exactly solvable many-body models indeed exhibit just that property [4,5]. However, it rests as well on a frankly crude and intuitive (but general) argument that macroscopic subvolumes of V could be geometrically reordered essentially independently of one another and thus that Ω_1 would have to be multiplicative over those subvolumes [6]. The purpose of the present work is to supply a stronger general basis for the claim of exponential multiplicity of distinct inherent structures in material systems.

Section II establishes on physical grounds a lower bound for Ω_1 that itself rises exponentially with N, so α in the right member of Eq. (1.2) must be greater than zero, if it exists. Section III establishes that this right member is bounded above, using the strategy of *reductio ad absurdum*. Section IV takes up the question of enumerating inherent structures in free space and concludes that if attractive forces are present (as is true for ''real'' material systems), then α must diverge to infinity as N/V goes to zero. Section V presents several concluding remarks, including some directed to polymeric substances and to mixtures.

II. LOWER BOUND

As in the preceding Introduction, attention will focus for the moment on the single-component case. Realistic interac-

tion potentials Φ that describe such systems are continuous and at least once differentiable away from nuclear confluences; furthermore, they are bounded below by $-BN$ for some $B > 0$ [7]. In the large system limit of interest here, the absolute minimum of Φ will correspond to some periodic crystal structure whose details (symmetry, unit cell dimensions, etc.) reflect the molecular shape and flexibility and the balance between intermolecular attractions and repulsions. Several alternative, less stable, crystal structures may also exist for the pure substance of interest; however, only the classical ground state (the absolute Φ minimum) need be considered for establishing a lower bound to $\ln \Omega_1$.

Place the N molecules into one of the permutationally equivalent absolute-minimum configurations. The resulting elastic solid may or may not entirely fill the finite available system volume V, depending on how the latter compares with the zero-pressure, zero-temperature volume of the N-molecule crystal. In either event let V_0 be the volume actually occupied by the crystal.

Divide V_0 into identical compact subvolumes v_0, of microscopic size, each containing on average n_0 molecules. The number of such subvolumes is

$$V_0/v_0 = N/n_0. \tag{2.1}$$

The intention is to choose v_0 sufficiently large (though still on the molecular scale) that a mechanically stable defect-containing rearrangement of molecules could be effected in each subvolume, without affecting the possibility of such rearrangement in any other subvolume. The type of crystal defect involved can vary according to the substance under consideration. In the case of atomic substances a nearby vacancy-interstitial pair (Frenkel defect) is the natural choice, resulting from lengthwise displacement of a short line of particles [8]. On the other hand, substances composed of large flexible molecules admit defects resulting from single molecular reorientation or internal motion [9].

Notice that we do not require the defects in separate subvolumes be noninteracting, but only that the interactions be sufficiently weak that the absence or presence of defects in all subvolumes be possibilities that are independent of one another. Elastic strains surrounding defects will propagate through the crystal medium causing defect-defect interactions, but these strain fields die off algebraically with distance [10]. Hence the independence assumption will place a lower limit on v_0 (and thus n_0).

Let γ be the number of distinguishable configurations that the defective state in v_0 can adopt. This might count the different relative positions of a vacancy-interstitial pair or the different ''unnatural'' but mechanically stable reconfigurings of a flexible molecule. In any event the number of undisturbed plus defective states considered for each subvolume is $1 + \gamma$. On account of subvolume independence, we thus consider the following number of distinguishable, mechanically stable configurations (inherent structures) for the N-particle system:

$$(1 + \gamma)^{V_0/v_0} \equiv \exp\{[n_0^{-1}\ln(1 + \gamma)]N\}. \tag{2.2}$$

Presumably this represents only a small subset of all distinguishable inherent structures for the N particles in fixed finite volume V, so we can write

$$\exp\{[n_0^{-1}\ln(1 + \gamma)]N\} \leqslant \Omega_1. \tag{2.3}$$

If the limit indicated earlier in Eq. (1.2) indeed exists, then the expression (2.3) implies

$$0 < n_0^{-1}\ln(1 + \gamma) \leqslant \alpha. \tag{2.4}$$

III. UPPER BOUND

The next task is to examine the implications of the possible violation of the limiting behavior in Eq. (1.2) due to greater-than-linear rise of $\ln \Omega_1$ with N. Suppose tentatively that the following large-N behavior (with positive N/V fixed) applies:

$$\ln \Omega_1 \sim f(N), \tag{3.1}$$

where

$$\lim_{N \to \infty} [N/f(N)] = 0. \tag{3.2}$$

This could arise, for example, if $f(N)$ were proportional to N^q, $q > 1$. Such behavior has significant consequences for the mean size of basins belonging to the system's inherent structures.

The configuration space content for a single molecule/particle can be written as $V\omega$. The first factor is attributable to center of mass translation, while the second factor is just the integral (between bounded limits) of the ν internal degrees of freedom. In the simple case of structureless particles ($\nu = 0$), ω is set to unity. The content of the multidimensional configuration space describing all N molecules/particles simultaneously is $(V\omega)^N$. The mean basin content emerges upon dividing this content by the number of basins

$$\frac{(V\omega)^N}{N!\Omega_1(N)}. \tag{3.3}$$

In order to interpret the expression (3.3) physically, it is useful to reexpress it in terms of a mean linear displacement l for each molecule/particle. Consequently Eq. (3.3) can alternatively be written in the form $(\omega l^3)^N$. The asymptotic large-N behavior tentatively postulated for Ω_1 then leads to the following result for l:

$$l^3(N) \sim (V/N)\exp[1 - f(N)/N]. \tag{3.4}$$

The postulated property (3.2) for $f(N)$ forces l to vanish in the large system limit ($N \to +\infty$, positive N/V fixed). This is physically unacceptable because it implies that arbitrarily small displacements in virtually any direction suffice to switch the system from one inherent structure to another. In particular this would render impossible phonon motions of finite amplitude in the crystalline state (no restoring forces), as well as kinetic arrest in nonergodic trapped glassy states (a common occurrence for amorphous substances). Conventional experience, however, indicates that l should remain positive and of the order of molecular dimensions in the large system limit. This can only happen if $f(N)$ is linear in N and in accord with Eq. (1.2), specifically

$$f(N) \sim \alpha N. \tag{3.5}$$

IV. DENSITY DEPENDENCE

The considerations presented in Secs. II and III force the conclusion that Ω_1 indeed rises exponentially with N at fixed positive density, i.e., that α in Eq. (1.2) is well defined. However, this leaves open the issues of how α depends on the substance under consideration and for any given substance how this parameter varies with density.

A particularly simple situation arises if the potential energy function Φ is homogeneous of degree $-n$, $n>3$. This obtains specifically when Φ is composed of purely repulsive inverse-power pair potentials

$$\Phi(\mathbf{r}_1,\ldots\mathbf{r}_N)=\sum_{i<j} \, (\sigma/r_{ij})^n. \qquad (4.1)$$

In this circumstance any inherent structure (local Φ minimum) at system volume V, with particle locations $\mathbf{r}_{1q},\ldots,\mathbf{r}_{Nq}$, transforms precisely to a corresponding inherent structure at volume V', with scaled particle locations $(V'/V)^{1/3}\mathbf{r}_{1q},\ldots,(V'/V)^{1/3}\mathbf{r}_{Nq}$. Consequently, α is density independent for this special case, though it may depend on exponent n.

The wider circumstance where Φ is not homogeneous evidently can lead to density dependence for the exponential rise rate parameter α. The exactly solvable one-dimensional model investigated by Häner and Schilling [5] possesses an α that declines monotonically with increasing pressure, i.e., with increasing density. Furthermore, Malandro and Lacks [11] have numerically investigated a Lennard-Jones-like three-dimensional model, establishing at least over a limited density range in finite systems that Ω_1 decreases with increasing density. Heuer has obtained similar results for the same model [12]. It should also be mentioned that analytic properties of the pairwise additive Gaussian core model also require that its Ω_1 decrease with increasing density [13]. While the present understanding cannot exclude the possibility that α might increase with density over a limited density range for some model potential, this would seem to be exceptional behavior.

The tendency for Ω_1, and thus α, to increase as density declines when attractive interparticle forces are present seems to have a straightforward explanation. Attractions have been observed in simulations to stabilize porous inherent structures in which the void space can adopt a wide variety of convoluted and multiconnected shapes [14,15]. Furthermore, the real substances Kr and N_2 can experimentally be prepared in analogous states as mesoporous solids [16] and the very low-density aerogels composed of SiO_2 provide a particularly dramatic related example [17]. The presence of substantial open space in these structures offers many opportunities for reconfiguring the particles into alternative mechanically stable arrangements, far exceeding in number those available at high density where particles interfere severely.

To strengthen this argument it is useful to consider the formation of inherent structures for N particles in free space, i.e., $V \rightarrow +\infty$. The very open and multiply branched structures produced by diffusion-limited aggregation processes [18] suggest that similar forms might be expected for free-space inherent structures. This in turn invalidates the basis on which the exponential rise rate of Ω_1 with N [Eq. (1.2)] has been established for fixed positive density.

An elementary, approximate, enumeration scheme for inherent structures in free space implies that Ω_1 rises more rapidly than as a simple exponential. Suppose in fact that the "typical" free-space inherent structure is indeed very open. Imagine constructing such arrangements particle by particle from an initial seed. At any intermediate stage, the number of distinct sites at which the next particle could be attached to the incomplete cluster would be roughly proportional to N', the number already in place. Therefore, we have ($K>0$)

$$\Omega_1(N'+1)\cong KN'\Omega_1(N'). \qquad (4.2)$$

Taking logarithms and treating the large variable N' as continuous, we have

$$d \ln \Omega_1(N')/dN'\cong\ln(KN'). \qquad (4.3)$$

This can be integrated to yield

$$\ln \Omega_1(N)\cong N \ln N+(\ln K-1)N+C, \qquad (4.4)$$

where C is an integration constant. Clearly this result contradicts the positive density presumption embodied in Eq. (1.2) and suggests a faster-than-exponential rise rate with increasing N.

A more insightful enumeration scheme than the crude one just presented might reveal that as particles are added, the previously emplaced "substrate" might not simply serve as a nearly rigid host, but be capable of new and distinct stable arrangements that could not exist without the additional particle. If such possibilities are present and sufficiently numerous, the estimate (4.4) above might actually be a significant underestimate. That could conceivably lead to the form (3.1) shown earlier with $f(N)$ proportional to N^q, $q>1$. However, without having to settle these technical details, we can safely conclude that for any three-dimensional model substance possessing attractive interparticle interactions, the parameter α must diverge to infinity as the density goes to zero.

V. DISCUSSION

The lower bound for α provided by Eq. (2.4) may prove to be very weak in many applications. In order to satisfy the defect-independence assumption on which that result is based, n_0 would probably have to be of order 10^2; assigning the value 6 to γ then might be reasonable [19]. Consequently, Eq. (2.4) would state

$$(\ln 7)/100=0.019\,459\,1 \ldots \leqslant\alpha. \qquad (5.1)$$

By contrast, Wallace [20] estimates that

$$\alpha\cong0.8 \qquad (5.2)$$

for a wide range of monatomic substances. Flexible organic molecules such as the fragile glass former ortho-terphenyl (OTP) appear to exhibit substantially larger α values; a simple calculation based on its measured heat capacity and heat of fusion suggests that [21]

$$\alpha(\text{OTP}) \cong 13.14. \qquad (5.3)$$

Linear polymeric substances may exhibit α's that increase roughly linearly with the degree of polymerization (numbers of monomer units), at fixed overall mass density, owing to backbone flexibility degrees of freedom. These discrepancies with Eq. (5.1) warrant searching in the future for more powerful bounds for α.

The focus of the foregoing arguments has been the total number of inherent structures, regardless of how they may differ in detail. However, it is also important to classify inherent structures according to one or more intensive ''order'' parameters and if possible to obtain their distribution with respect to these parameters. A particularly important case involves ϕ, the potential energy per particle of the inherent structures, because this leads to an especially simple expression for the free energy of the many-particle system [3,6]. Given the validity of Eq. (1.2) and assuming the continuity of the asymptotic distribution with respect to ϕ, it is inevitable that this distribution of distinguishable inherent structures have the form [3,6]

$$\exp[N\sigma(\phi)], \quad \sigma \geq 0. \qquad (5.4)$$

Although the developments in the Secs. II–IV have been restricted to single-component systems, mixtures also deserve examination. In the general case involving components $1, \ldots, \nu$, Eq. (1.1) generalizes to

$$\Omega(N_1, \ldots N_\nu, V) = (\Pi N_\mu!)\Omega_1(N_1, \ldots N_\nu, V), \qquad (5.5)$$

with Ω_1 expected asymptotically to rise exponentially with the total number of particles (all densities N_μ/V held fixed). However, because the components are distinguishable, the exponential rise rate quantity α should be larger than its single-component relatives on account of mixing entropy effects.

A concrete example serves to illustrate the last point. Let $\alpha(N_2)$ be the exponential rise rate quantity for pure molecular nitrogen. Carbon monoxide has a small molecular dipole moment [22] and has nearly the same molecular size as the dipole-moment-free nitrogen molecule [23]. Consequently, CO should be able freely and stably to substitute for N_2 in any inherent structure for the latter. Taking due account of the two distinguishable orientations available for each substituting CO, one estimates α for the N_2-CO mixture to be

$$\alpha \cong \alpha(N_2) + x \ln 2 - x \ln x - (1-x)\ln(1-x), \qquad (5.6)$$

where x is the mole fraction of CO in the mixture.

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