

Inherent structure formalism for quantum systems

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A theoretical procedure in classical statistical mechanics, using configurational mapping to distinguish particle packing effects from vibrational smearing effects, has previously been developed for understanding short-range order in condensed phases. The present paper exhibits the generalization to quantum systems with arbitrary spin, but with spin-independent Hamiltonians. Remarks are included indicating how the popular path-integral Monte Carlo method for simulating quantal many-body systems via digital computer can be adapted to determine inherent packing structure. It is predicted that quantum effects in both liquid and solid phases tend to produce inherent structures that are more porous, defective, and higher in energy than their classical counterparts.

I. INTRODUCTION

The inherent structure approach in classical statistical mechanics was introduced as a tool for understanding structure, kinetics, and phase change in condensed matter.¹⁻⁴ It is based on a precise separation of atomic (or molecular) packing effects from vibrational motion effects within multidimensional potential energy "basins" surrounding the mechanically stable packing configurations. This approach has been instrumental in identifying temperature-independent packing order in stable liquids.⁵⁻⁷ It has led to a "mirror image" of the Lindemann melting criterion, which now offers a freezing criterion for atomic liquids.⁸ It has also clarified the nature of supercooled liquids^{9,10} and low-temperature amorphous solids, where for the latter (in connection with molecular dynamics computer simulation) bistable degrees of freedom that could produce two-level tunneling systems have been identified and characterized.^{3,11}

This paper has as its main objective an extension of the inherent structure approach to the quantum regime. There is ample motivation behind this objective. The striking and peculiar properties of He³ and He⁴ alone justify seeking the extension.^{12,13} But in addition, it is important to have a theoretical basis for understanding supercooled liquid hydrogen.¹⁴ Various chemical phenomena also warrant the quantum generalization of the inherent structure formalism; this is especially true where hydrogen nuclear motions are involved as in acid-base equilibria and in tautomerism.¹⁵ Finally, the extension would facilitate quantitative description of isotope effects in hydrogen-bonded crystals, including some ferroelectrics.¹⁶

Section II describes the mass-weighted steepest-descent mapping to potential minima that underlies the method. This is the same mapping required in the classical limit,¹⁻⁴ but now it must be applied to the quantum mechanical density matrix. Section III demonstrates how the quantum mechanical canonical partition function must be transformed in order to effect separation of packing geometrical attributes from those due to intrabasin vibrations. Section IV takes up the issue of path-integral representations that recently have been a popular topic in quantum statistics, and indicates how the corresponding quantum simulations via

digital computer could be adapted to reveal quantum inherent structure. Finally, Sec. V discusses several applications.

II. MAPPING TO MINIMA

The case to be explicitly examined involves a large number N of identical particles, all of mass m , whose positions will be denoted by $\mathbf{r}_1 \cdots \mathbf{r}_N$. These particles will be structureless except for a spin degree of freedom, and $s_1 \cdots s_N$ will represent the projections of the respective spin angular momenta along some fixed direction.

A movable piston will be included as part of the system's dynamical description in order to ensure constant pressure conditions. The piston location will be specified by a scalar variable x_0 . Piston mass m_0 will be of order Nm , i.e., a macroscopic quantity.

The applications envisioned for the formalism will identify $\mathbf{r}_1 \cdots \mathbf{r}_N$ as positions of atomic nuclei which interact among themselves on a ground-electronic-state potential hypersurface $\Phi_0(\mathbf{r}_1 \cdots \mathbf{r}_N)$. They also interact with the piston and the fixed container walls via some other potential function $U(x_0, \mathbf{r}_1 \cdots \mathbf{r}_N)$. The total potential energy for the system comprising piston plus particles will be

$$\Phi(x_0, \mathbf{r}_1 \cdots \mathbf{r}_N) = \Phi_0(\mathbf{r}_1 \cdots \mathbf{r}_N) + U(x_0, \mathbf{r}_1 \cdots \mathbf{r}_N) + pV(x_0). \quad (2.1)$$

The last term on the right represents "spring loading" on the piston, with p the constant pressure applied to the system, and $V(x_0)$ the system volume. Notice that all contributions to Φ have been assumed to be spin independent.

The Hamiltonian operator for the composite system of piston plus particles is obvious:

$$\mathbf{H} = -(\hbar^2/2m_0) \frac{\partial^2}{\partial x_0^2} - (\hbar^2/2m) \sum_{j=1}^N \nabla_j^2 + \Phi(x_0, \mathbf{r}_1 \cdots \mathbf{r}_N). \quad (2.2)$$

Its exact eigenfunctions and eigenvalues will be denoted by ψ_n and E_n , respectively. If $p > 0$ there will be no continuum states, and the ψ_n should then constitute a complete set.

The state of the many-body system at time t is specified by the (unaveraged) density matrix, which in space-spin representation is¹⁷

$$\rho(\mathbf{R}, \mathbf{s} | \mathbf{R}', \mathbf{s}'; t) = \sum_{a,b} C_a^* C_b \psi_a^*(\mathbf{R}, \mathbf{s}) \psi_b(\mathbf{R}', \mathbf{s}') \times \exp[(i/\hbar)(E_a - E_b)t], \quad (2.3)$$

where for notational simplicity

$$\mathbf{R} \equiv (x_0, \mathbf{r}_1 \cdots \mathbf{r}_N), \quad \mathbf{s} \equiv (s_1 \cdots s_N), \quad (2.4)$$

and where the constants C_a convey the initial condition. The time-dependent configurational probability for the composite system can be obtained by summing diagonal elements of the density matrix over spin variables:

$$P(\mathbf{R}, t) = \sum_{\mathbf{s}} \rho(\mathbf{R}, \mathbf{s} | \mathbf{R}, \mathbf{s}; t). \quad (2.5)$$

The immediate objective is to map this function onto a discrete set of probabilities associated with the local minima of Φ in the $(3N + 1)$ -dimensional configurational space for the composite system.

Just as in the constant-pressure classical version,¹⁰ the mapping will be effected through the mass-weighted descent equations:

$$m_0 \frac{dx_0}{du} = -\frac{\partial \Phi}{\partial x_0}, \quad m \frac{dr_j}{du} = -\nabla_j \Phi. \quad (2.6)$$

With the exceptions of a zero-measure subset, any system configuration \mathbf{R} is mapped uniquely onto the configuration \mathbf{R}_α of a local minimum of Φ . Technically this requires using \mathbf{R} as the initial ($u = 0$) condition for coupled Eqs. (2.6), then using their solution $\mathbf{R}(u), u > 0$ as the connection to \mathbf{R}_α :

$$\lim_{u \rightarrow \infty} \mathbf{R}(u) = \mathbf{R}_\alpha. \quad (2.7)$$

The set of all initial configurations \mathbf{R} that map onto a given \mathbf{R}_α defines the basin B_α surrounding minimum α ; and the union of all B_α essentially spans the entire available configuration space for the composite system.

In the large system limit the number Ω of Φ minima is expected on general grounds² to increase with N in the following way:

$$\ln \Omega \sim \ln(N!) + \nu N, \quad (2.8)$$

where ν is a positive constant of order unity. The $N!$ accounts for the obvious fact that minima fall into equivalence classes within each of which members differ only by permutation of identical particles. The quantity ν measures the number of geometrically distinct particle packings (Φ minima), and can be expected to depend on p .

The probabilities $P_\alpha(t)$ that the quantum mechanical system is to be found in each of the basins B_α at time t can be written thus:

$$P_\alpha(t) = \int_{B_\alpha} d\mathbf{R} P(\mathbf{R}, t). \quad (2.9)$$

If the density matrix is properly normalized, then

$$\sum_{\alpha} P_\alpha(t) = 1, \quad (2.10)$$

where the sum includes all Ω basins.

The solutions to Eq. (2.6) always move downward in potential energy:

$$\Phi[\mathbf{R}(u_1)] > \Phi[\mathbf{R}(u_2)] \quad (u_1 < u_2), \quad (2.11)$$

unless the starting point itself were a minimum. If m_0 were equal to the particle mass m , each solution $\mathbf{R}(u)$ would be a steepest-descent trajectory on the Φ hypersurface. But since

$$m_0 \gg m \quad (2.12)$$

there is a separation of scales in the virtual time variable u . The first stage in the evolution of $\mathbf{R}(u)$ corresponds substantially to minimizing Φ with respect to particle coordinates at fixed x_0 (i.e., fixed volume). Only much later in u can the sluggish variable x_0 change, during the course of which the particle positions continue to remain close to constrained Φ minima for the momentary x_0 value.

III. CANONICAL PARTITION FUNCTION

The averaged density matrix for an isothermal, isobaric ensemble at temperature $T = (k_B \beta)^{-1}$ has the form

$$\rho_{\text{eq}}(\mathbf{R}, \mathbf{s} | \mathbf{R}', \mathbf{s}') = \sum_n \psi_n^*(\mathbf{R}, \mathbf{s}) \psi_n(\mathbf{R}', \mathbf{s}') \exp[\beta(G - E_n)]. \quad (3.1)$$

Here G is the Gibbs free energy for the composite system given by the partition function Z :

$$Z(\beta, p) = \exp[-\beta G(\beta, p)] = \text{Tr}[\exp(-\beta \mathbf{H})] = \sum_n \exp[-\beta E_n(p)]. \quad (3.2)$$

All thermodynamic properties for the system can be extracted from G by standard formulas.¹⁸

It is useful to express the trace in Eq. (3.2) explicitly in the ψ_n basis, and to break the configurational integration into portions for each basin:

$$Z(\beta, p) = \sum_{\alpha} \int_{B_\alpha} d\mathbf{R} \sum_n \sum_s \psi_n^*(\mathbf{R}, \mathbf{s}) \psi_n(\mathbf{R}, \mathbf{s}) \exp(-\beta E_n). \quad (3.3)$$

Integrals for permutation-equivalent basins are identical, so to avoid redundancy an alternative form is

$$Z(\beta, p) = \sum_{\alpha}' \int_{B_\alpha} d\mathbf{R} \left[N! \sum_n \sum_s \psi_n^*(\mathbf{R}, \mathbf{s}) \psi_n(\mathbf{R}, \mathbf{s}) \times \exp(-\beta E_n) \right], \quad (3.4)$$

where the primed summation includes only one of each geometrically distinct type of basin.

Let Φ_α denote the value of Φ at the bottom of the basin B_α :

$$\Phi_\alpha = \Phi(\mathbf{R}_\alpha). \quad (3.5)$$

Consequently Eq. (3.4) leads to the following:

$$Z(\beta, p) = \sum_{\alpha}' \exp[-\beta \Phi_\alpha(p) - \beta F_{\nu\alpha}(\beta, p)], \quad (3.6)$$

where $F_{v\alpha}$ represents a "vibrational" free energy for basin B_α ;

$$\exp(-\beta F_{v\alpha}) = \int_{B_\alpha} d\mathbf{R} \left\{ N! \sum_n \sum_s \psi_n^*(\mathbf{R}, \mathbf{s}) \psi_n(\mathbf{R}, \mathbf{s}) \right. \\ \left. \times \exp[\beta(\Phi_\alpha - E_n)] \right\}. \quad (3.7)$$

Notice that this last quantity receives contributions from all eigenstates of \mathbf{H} . In particular this is true even when the eigenvalue E_n lies below Φ_α , but for such states the system's presence within the classically disallowed B_α is due only to quantum mechanical tunneling and thus has little weight.

In view of the very large number of inequivalent basins a statistical description is natural. Just as in the classical version¹⁻⁴ it is useful to classify basins by depth on a per-particle basis:

$$\phi = \Phi_\alpha / N. \quad (3.8)$$

Denote the unit step function by $u(x)$:

$$u(x) = 0 \quad (x < 0) \\ = 1 \quad (x \geq 0). \quad (3.9)$$

Then define an intensive basin-enumeration function σ by

$$\sigma(\phi) = \lim_{\epsilon \rightarrow 0} \lim_{N \rightarrow \infty} N^{-1} \ln \left[\sum_\alpha u(\Phi_\alpha - N\phi + N\epsilon) \right. \\ \left. \times u(N\phi + N\epsilon - \Phi_\alpha) \right], \quad (3.10)$$

wherein the limits are to be carried out at constant p . As a consequence,

$$\exp[N\sigma(\phi)] d\phi \quad (3.11)$$

represents (in the large- N asymptotic limit) the number of minima in the depth-per-particle range $\phi \pm \frac{1}{2}d\phi$. Note should be taken of the identity

$$\nu = \max_{(\phi)} \sigma(\phi), \quad (3.12)$$

where ν was introduced in Eq. (2.8) above.

A mean vibrational free energy per particle \hat{f}_v can similarly be defined for basins with depth ϕ :

$$\hat{f}_v(\beta, \phi) = -\beta^{-1} \lim_{\epsilon \rightarrow 0} \lim_{N \rightarrow \infty} N^{-1} \ln \langle \exp(-\beta F_{v\alpha}) \rangle_{\phi, \epsilon}, \\ \langle \exp(-\beta F_{v\alpha}) \rangle_{\phi, \epsilon} \\ = \left[\sum_\alpha u(\Phi_\alpha - N\phi + N\epsilon) u(N\phi + N\epsilon - \Phi_\alpha) \right]^{-1} \\ \times \sum_\alpha u(\Phi_\alpha - N\phi + N\epsilon) u(N\phi + N\epsilon - \Phi_\alpha) \\ \times \exp(-\beta F_{v\alpha}). \quad (3.13)$$

Both σ and \hat{f}_v depend implicitly on external pressure p .

Armed with the definitions of σ and \hat{f}_v , it becomes possible to convert expression (3.6) for Z , valid asymptotically in the large-system limit, into a simple quadrature over the depth parameter ϕ :

$$Z(\beta, p) \sim \int d\phi \exp\{N[\sigma(\phi) - \beta \hat{f}_v(\beta, \phi)]\}. \quad (3.14)$$

Since N is large, this quadrature will be dominated in leading order in N by the immediate neighborhood of the integrand maximum, say at $\phi = \phi_m(\beta, p)$. Consequently the Gibbs free energy may be obtained from the following simple but asymptotically exact formula:

$$-\beta G(\beta, p) \sim N\{\sigma(\phi_m) - \beta \hat{f}_v(\beta, \phi_m)\}. \quad (3.15)$$

Phase transitions are associated with singularities of ϕ_m as a function of β and p . The quantity ϕ_m identifies the depth of those basins within which the system is almost certain to be found at the ambient temperature and pressure.

Except for a trivial difference regarding definition of the vibrational free energy, the representation of Z as a ϕ quadrature is the same as previously exhibited for the classical statistical mechanical regime.¹⁻⁴ Indeed the basin enumeration function σ is identical in quantum and in classical contexts. All quantum effects reside in the vibrational free energy \hat{f}_v whether they are due to zero-point motion, quantum diffraction effects, spin, or statistics.

IV. PATH-INTEGRAL REPRESENTATION

The inherent structure for the quantum system is given by the set of probabilities $P_\alpha(t)$ defined by Eq. (2.9). These in turn can be obtained by sampling diagonal elements of the density matrix in coordinate representation and by applying the mass-weighted steepest-descent mapping. When thermal equilibrium obtains the density matrix has form (3.1), or equivalently

$$\rho_{\text{eq}}(\mathbf{R}, \mathbf{s} | \mathbf{R}', \mathbf{s}') = Z^{-1} \langle \mathbf{R}, \mathbf{s} | \exp(-\beta \mathbf{H}) | \mathbf{R}', \mathbf{s}' \rangle, \quad (4.1)$$

and the basin probabilities have time-independent values $P_\alpha^{(\text{eq})}(\beta)$.

Path-integral methods based on the Feynman formalism¹⁹ have become a popular and useful approach to generating the equilibrium density matrix. Recent applications have included numerical studies of models for noble gas clusters,²⁰ liquid and solid helium,²¹ liquid water,²² and solvated electrons.²³ On account of its frequent use in computer simulations such as these, the following product identity bears reexamination:

$$\langle \mathbf{R}, \mathbf{s} | \exp(-\beta \mathbf{H}) | \mathbf{R}', \mathbf{s}' \rangle \\ \equiv \langle \mathbf{R}, \mathbf{s} | [\exp(-\beta \mathbf{H}/l)]^l | \mathbf{R}', \mathbf{s}' \rangle, \quad (4.2)$$

where l is any positive integer. If l is sufficiently large, the individual factors can explicitly be evaluated as follows²⁴⁻²⁶:

$$\langle \mathbf{R}, \mathbf{s} | \exp(-\beta \mathbf{H}/l) | \mathbf{R}', \mathbf{s}' \rangle \\ \equiv \frac{1}{N!} \left[\frac{1}{\hbar} \left(\frac{ml}{2\pi\beta} \right)^{1/2} \right]^{3N} \\ \times \exp\{ -(\beta/2l) [\Phi(\mathbf{R}) + \Phi(\mathbf{R}')] \} \delta(\mathbf{x}_0 - \mathbf{x}'_0) \\ \times \sum_P (\pm 1)^{|P|} \prod_{j=1}^N \exp[- (ml/2\beta\hbar^2) (\mathbf{r}'_j - \mathbf{r}_{Pj})^2] \\ \times \delta_K(s'_j, s_{Pj}), \quad (4.3)$$

where we have taken full account of particle spin. In this expression P represents the permutation operator for parti-

cle indices, and the parity of a given permutation has been denoted by $|P|$; upper and lower signs refer, respectively, to bosons and to fermions. The Dirac and Kronecker delta functions have been symbolized by δ and δ_K , respectively. That x_0 and x'_0 must be equal in the asymptotic form (4.3) stems from the large mass m_0 of the piston.

When the propagator (4.3) is employed to evaluate the partition function, one obtains

$$Z = \text{Tr}\{\exp(-\beta H/l)\} \\ = \sum_{\mathbf{s}^{(1)}, \dots, \mathbf{s}^{(l)}} \int d\mathbf{R}^{(1)} \dots \int d\mathbf{R}^{(l)} \prod_{i=1}^l \langle \mathbf{R}^{(i)}, \mathbf{s}^{(i)} \rangle$$

$$Z = \frac{1}{N!} \left\{ \frac{1}{\hbar} \left[\frac{ml}{2\pi\beta} \right]^{3N} \right\}^l \int dx_0 \exp[-\beta p V(x_0)] \sum_P (\pm 1)^{|P|} (2S+1)^{N_P(P)} \int d\mathbf{R}^{(1)} \dots \int d\mathbf{R}^{(l)} \exp\left\{ -(\beta/l) \right. \\ \left. \times \sum_{i=1}^l [\Phi_0(\mathbf{R}^{(i)}) + U(\mathbf{R}^{(i)})] - (ml/2\beta\hbar^2) \sum_{j=1}^N \left[\sum_{i=1}^{l-1} (\mathbf{r}_j^{(i+1)} - \mathbf{r}_j^{(i)})^2 + (\mathbf{r}_j^{(1)} - \mathbf{r}_j^{(l)})^2 \right] \right\}. \quad (4.5)$$

In this expression the permutation operator P acts only on the l th "monomers" to produce extended "exchange" polymer rings; the total number of cyclic polymers for a given permutation has been denoted by $N_P(P)$.

The spatial distribution of sets of N monomer units that is implicit in the partition function (4.5), along with the piston coordinates x_0 , is the input required for the steepest-descent mapping, Eq. (2.6). Monte Carlo procedures²⁰⁻²⁶ designed to generate these quantum mechanical distributions could be straightforwardly augmented with numerical mapping to potential minima to yield the inherent structure for the system of interest.

In the very low temperature limit the path-integral approach just examined becomes cumbersome since l must be taken to be very large. At absolute zero where only the ground state contributes, alternative methods exist for numerically generating the appropriate configurational distribution. Notable among these is the Green's function Monte Carlo procedure,^{27,28} which could likewise supply the necessary input for steepest-descent mapping. However, for atomic or molecular systems at intermediate temperatures where quantum corrections to classical statistical behavior should be moderate, path-integral Monte Carlo simulations augmented with configurational mapping should be useful for studying local order.

V. DISCUSSION

In anticipation of brute-force computational studies, it may be useful to list some expectations about quantum effects on inherent structure.

One of the obvious phenomena stemming from quantization is reduction in density, at a given pressure, due to quantum zero-point motions. This is very evident in the liquid and crystal phase densities of the helium isotopes, less so for those of neon, compared to those of the heavier noble gases. Configurational mapping at $p = 1$ bar, say, undoubtedly would produce more porous (i.e., vacancy containing)

$$\times \exp(-\beta H/l) | \mathbf{R}^{(i+1)}, \mathbf{s}^{(i+1)} \rangle, \quad (4.4)$$

wherein $l+1 \equiv 1$. It can be recognized that the resulting multiple integrals might be interpreted as describing thermal behavior of cyclic polymers.^{25,26} These polymers each contain a number of monomer units equal to l or a multiple thereof (depending on the permutation involved), they have alternating weights for fermions, and their interactions consist of harmonic-spring "bonds" as well as particle potentials between monomers with equal indices i .

The explicit form (4.3) shows that spins must be identical around any cyclic polymer, and that only a single piston variable appears. Consequently, Z can be put into the following form:

packings in the case of low-mass substances compared to high-mass substances. If a common scalable potential were involved, such as the Lennard-Jones interaction for the noble gases, then the enumeration function σ would be unchanged, but ϕ_m in Eq. (3.15) would manifest mass dependence on account of the underlying influence of the vibrational free energy \hat{f}_v . In particular decreasing mass and increasing packing porosity in most instances should have the effect of increasing ϕ_m at fixed p and β .

As regards the inherent structure of quantum crystals it seems unavoidable that small (but nonvanishing) contributions from defective packings would persist even at absolute zero. That is, tunneling carries the crystalline system out of basins corresponding to absolute potential minima (with perfect particle order) into nearby and slightly higher basins whose packings contain point defects such as vacancies and interstitials. In the case of long-range ordered hydrogen-bonded crystals, defects in the form of concerted proton or deuteron displacements around closed hydrogen-bond loops are possible, and should become especially likely under elevated pressure as double-minimum bond potentials are flattened.^{29,30}

Finally, there is the important subject to consider of metastable condensed phases for quantum systems. This includes supercooled liquids such as those of H_2 and Ne , as well as amorphous solid deposits that might be formed from some of the lighter elements. A systematic procedure has been developed^{9,10} in the classical limit for using the configuration-space mapping approach to describe metastable phases, based upon suitable basin subsets. It appears that no difficulty would arise in extending that work to the quantum regime along the lines discussed in previous sections of this paper.

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