

Distinguishing Vibrational and Structural Equilibration Contributions to Thermal Expansion

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Geometric attributes of a many-body-system potential energy function suggest a natural description of that system in terms of inherent structures (local potential minima), and intra-basin vibrational displacements away from those discrete structures. This description is applied herein to the isobaric thermal expansion property (α). Starting with the virial form of the pressure equation of state, two distinct contributions to α can be unambiguously identified. The first (α_{vib}) arises from intra-basin anharmonic thermal vibrations; the second (α_{str}) stems from thermally induced structural shifts in basin occupancy. Only α_{vib} appears for nondefective crystals, and for glasses below their T_g 's. An approximate analysis for liquid water suggests that α_{str} alone manifests a liquid-phase density maximum, thought shifted to slightly higher temperature than the observed density maximum at 4 °C.

I. Introduction

Isobaric thermal expansion (α) is a basic materials property that measures volume (V) response in a closed system under constant pressure (p) to an incremental change in temperature (T):

$$\alpha = (\partial \ln V / \partial T)_p \quad (1.1)$$

The fact that α usually is nonvanishing can technologically be either an advantage or a liability. On one hand, thermal expansion in liquids and in solids, respectively, permits the construction and use of thermometers, and bimetallic strips for thermostats. On the other hand, devices or instruments with close dimensional tolerances (e.g., optical systems, computer hard-disk storage systems) as well as those required to operate over a wide temperature range could be seriously compromised in their operation by unwanted, or uncompensated, thermal expansion.

Connections between atomic-level materials structure and interactions and the macroscopic quantity α become especially intriguing in the case of those few (but important) substances exhibiting negative α 's. Solid-state examples of this anomalous behavior include ice Ih at low temperature,¹ cubic ZrW₂O₈,² and amorphous SiO₂.³ The collection of liquids with negative α contains superfluid HeII just below its λ transition,⁴ equilibrium-state and supercooled water below 4 °C,^{5,6} and the binary compound In₂Te₃.⁷

The theoretical approach adopted in the following focuses on the multidimensional configuration-space geometry of the potential energy function Φ for any material of interest. The "rugged landscape" presented by the Φ hypersurface in this space naturally divides into "basins of attraction," one surrounding each of the many local Φ minima ("inherent struc-

tures"). The development below shows that α contains two distinct contributions, an intra-basin (vibrational) part and an interbasin (structural equilibration) part. This separation has direct relevance to glass-forming liquids: Cooling through the glass transition temperature essentially produces a discontinuity in α owing to kinetic arrest of the structural relaxation contribution. It should be noted in passing that the isolation of vibrational and structural parts in α detailed below is analogous to a corresponding separation procedure that has been developed for isothermal compressibility.⁸

The initial portion of our analysis employs classical statistical mechanics, in the interests of presentation clarity and economy. In fact, the following Section II further restricts attention to classical statistical mechanical models comprising structureless spherical particles with additive interactions. Section III considers application of the approach to three such models that have enjoyed some measure of theoretical popularity: the inverse-power family of models,⁹ the hard sphere model,¹⁰ and the Gaussian core model,¹¹ the last of which displays a region of negative α . Section IV extends the analysis of Section II to include polyatomic molecules and nonadditive interactions. Section V outlines the manner in which proper quantum statistics must be invoked, an important consideration for solids at low temperature and for any substance with high-frequency intramolecular vibrational modes. Section VI presents an analysis of the vibration versus structural equilibration separation for liquid water. Conclusions and discussion of several issues raised by the present study appear in the final Section VII.

II. Simple Spherically Symmetric Particles

Initially we shall consider the case of a closed, thermostatted system containing N_1 particles of species 1, ..., N_ν particles of species ν , with

$$N = \sum_{\nu=1}^{\nu} N_{\nu} \quad (2.1)$$

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These N particles are confined to volume V by suitable repelling walls; V will eventually be allowed to fluctuate (movable walls), but external forces on the walls will be present to maintain the system at fixed pressure p . Interactions in the system can be designated with a two-part potential energy function Φ as follows:

$$\Phi(\mathbf{r}_1 \dots \mathbf{r}_N, V) = \Phi_o(\mathbf{r}_1 \dots \mathbf{r}_N) + \Phi_w(\mathbf{r}_1 \dots \mathbf{r}_N, V) \quad (2.2)$$

where $\mathbf{r}_1 \dots \mathbf{r}_N$ represent particle positions, Φ_o is the translation and rotation invariant collection of interactions among the particles, and Φ_w is the set of particle-wall interactions.

If the N -particle system is in a time-independent state, either at thermal equilibrium or in an indefinitely-long-lived metastable state, the Clausius virial theorem¹² applies. It asserts the following identity:

$$\frac{3}{2} N k_B T = - \frac{1}{2} \sum_{i=1}^N \langle \mathbf{F}_i \cdot \mathbf{r}_i \rangle \quad (2.3)$$

where k_B is Boltzmann's constant,

$$\mathbf{F}_i = -\nabla_i \Phi \equiv \mathbf{F}_{oi} + \mathbf{F}_{wi} \quad (2.4)$$

is the total force due to all interactions acting on particle i , and $\langle \dots \rangle$ indicates a time or ensemble average. Force terms in eq 2.3 attributable to wall interaction Φ_w can be identified as combining to give $(3/2)pV$, so virial relation (2.3) becomes:

$$pV = N k_B T + \frac{1}{3} \sum_{i=1}^N \langle \mathbf{F}_{oi} \cdot \mathbf{r}_i \rangle \quad (2.5)$$

Assume now that Φ_o consists only of additive spherical pair interactions:

$$\Phi_o = \sum_{i=2}^N \sum_{j=1}^{i-1} \nu_{\gamma\delta}(r_{ij}) \quad (2.6)$$

Here γ and δ denote the species of particles i and j , respectively. Under these special circumstances eq 2.5 undergoes further reduction to the following form:¹³

$$p = \rho k_B T - (2\pi\rho^2/3) \sum_{\gamma, \delta=1}^{\nu} x_\gamma x_\delta \int_0^\infty r^3 v'_{\gamma\delta}(r) g_{\gamma\delta}^{(2)}(r) dr \quad (2.7)$$

Here we have set

$$\begin{aligned} \rho &= N/V \text{ (total number density)} \\ x_\gamma &= N_\gamma/N \text{ (mole fraction of species } \gamma) \end{aligned} \quad (2.8)$$

and the $g_{\gamma\delta}^{(2)}$ are the pair correlation functions for γ, δ species of particle pairs.

Apply the differential operator $(\partial/\partial T)_p$ to both members of eq 2.7. By using the definition 1.1 for α , the result may be transformed into an expression for that quantity:

$$\alpha = (2p - \rho k_B T)^{-1} \{ \rho k_B - (2\pi\rho^2/3) \sum_{\gamma, \delta=1}^{\nu} x_\gamma x_\delta \int_0^\infty r^3 v'_{\gamma\delta}(r) [\partial g_{\gamma\delta}^{(2)}(r)/\partial T]_p dr \} \quad (2.9)$$

In the absence of any pair interactions, the N -particle system would be an ideal gas mixture, and the right member of this last expression for α reduces simply to T^{-1} .

To distinguish vibrational from structural equilibration contributions to α in eq 2.9, it is necessary to invoke a constant pressure steepest-descent mapping in the multidimensional space spanned by all particle coordinates $\mathbf{r}_1 \dots \mathbf{r}_N$ and the volume, V . Define the "potential enthalpy" function as follows:

$$\Psi(\mathbf{r}_1 \dots \mathbf{r}_N, V) = \Phi(\mathbf{r}_1 \dots \mathbf{r}_N, V) + pV \quad (2.10)$$

Steepest-descent trajectories on the Ψ hypersurface are defined as solutions $\mathbf{r}_i(s) \dots V(s)$ to the simultaneous equations ($s \geq 0$):^{14,15}

$$\begin{aligned} d\mathbf{r}_i(s)/ds &= -\nabla_i \Psi[\mathbf{r}_i(s) \dots V(s)] \quad (1 \leq i \leq N) \\ dV(s)/ds &= -\partial \Psi[\mathbf{r}_i(s) \dots V(s)]/\partial V \end{aligned} \quad (2.11)$$

In the $s \rightarrow \infty$ limit, these trajectories (only with zero-measure exceptions) carry any initial system configuration to a local Ψ minimum. The set of all configurations that map to the same local Ψ minimum l defines the basin B_l for that minimum.

Let $P_l(T, p)$ denote the probability that basin B_l is occupied by the configuration space point describing the N -particle system. Each of the pair correlation functions $g_{\gamma\delta}^{(2)}$ amounts to a weighted average of contributions $g_{\gamma\delta l}^{(2)}$ from the individual basins:

$$g_{\gamma\delta}^{(2)}(r) = \sum_l P_l g_{\gamma\delta l}^{(2)}(r) \quad (2.12)$$

This equation makes explicit the relationship between equilibrium liquid structure (i.e. $g_{\gamma\delta}^{(2)}$) and the manner in which the underlying landscape is explored (i.e. P_l). Differentiating eq 2.12, we have

$$[\partial g_{\gamma\delta}^{(2)}(r)/\partial T]_p = \sum_l P_l [\partial g_{\gamma\delta l}^{(2)}(r)/\partial T]_p + \sum_l (\partial P_l/\partial T)_p g_{\gamma\delta l}^{(2)}(r) \quad (2.13)$$

The first sum on the right side of the last equation is a weighted sum of intra-basin temperature variations for the $g_{\gamma\delta l}^{(2)}$ owing to increased intensity of vibrational motions as T rises. The second sum on the right side arises from shifting equilibrium between basins as temperature varies. Consequently these sums can be identified respectively as distinct "vibrational" and as "structural equilibration" effects. In a low-temperature crystalline solid, only intra-basin vibrational motions (possibly anharmonic) are expected to occur within the basins corresponding to the absolute Ψ minimum, so only the first sum in eq 2.13 would be nonvanishing.

Inserting eq 2.13 into eq 2.9 induces the desired separation for α . Specifically, we have

$$\alpha = \alpha_{\text{vib}} + \alpha_{\text{str}} \quad (2.14)$$

where

$$\begin{aligned} \alpha_{\text{vib}} &= (2p - \rho k_B T)^{-1} \{ \rho k_B - (2\pi\rho^2/3) \sum_{\gamma, \delta=1}^{\nu} x_\gamma x_\delta \sum_l P_l \int_0^\infty r^3 v'_{\gamma\delta}(r) [\partial g_{\gamma\delta l}^{(2)}(r)/\partial T]_p dr \} \\ \alpha_{\text{str}} &= (2p - \rho k_B T)^{-1} \{ - (2\pi\rho^2/3) \sum_{\gamma, \delta=1}^{\nu} x_\gamma x_\delta \sum_l (\partial P_l/\partial T)_p \int_0^\infty r^3 v'_{\gamma\delta}(r) g_{\gamma\delta l}^{(2)}(r) dr \} \end{aligned} \quad (2.15)$$

and

$$\alpha_{\text{str}} = -[2\pi\rho^2/3(2p - \rho k_{\text{B}}T)] \sum_{\gamma,\delta=1}^{\nu} x_{\gamma}x_{\delta} \sum_l \int_0^{\infty} r^3 v'_{\gamma\delta}(r) (\partial P_l / \partial T)_p g_{\gamma\delta}^{(2)}(r) dr \quad (2.16)$$

III. Specific Model Applications

The next step is to review the results of the preceding Section II in the context of three specific models. Each of the three involves just a single component whose particles are structureless and spherically symmetric. The interparticle interactions operative in each conform to the additivity assumption expressed earlier in eq 2.6.

A. Inverse Power Model. This case is defined by the generic pair potential ($n > 3$)

$$v(r) = \epsilon(\sigma/r)^n \quad (3.1)$$

where ϵ and σ are positive energy and length parameters, respectively. The simple form of v implies that nonideal parts of thermodynamic functions depend on temperature and density only through a single scaling variable that contains both.⁹ In particular, the pressure equation of state takes the following form:

$$\frac{p}{\rho k_{\text{B}}T} = 1 + q_n(\epsilon\sigma^n \rho^{n/3}/k_{\text{B}}T) \quad (3.2)$$

The dimensionless nonideality function q_n will vary with n certainly, and will satisfy the conditions

$$\begin{aligned} q_n(0) &= 0 \\ q_n(u) &> 0 \quad (u > 0) \end{aligned} \quad (3.3)$$

and will possess a set of singular points on the positive real axis associated with phase transitions. The latter include the melting and freezing points and, at least for some n values, singular points associated with FCC \leftrightarrow BCC crystal transitions.^{16,17}

Upon differentiating expression (3.2), one concludes that thermal expansion for the inverse power model must have the form:

$$\alpha = \left[\frac{1 + q_n(u) - uq'_n(u)}{1 + q_n(u) + (n/3)uq'_n(u)} \right] \frac{1}{T} \quad (3.4)$$

$$u = \epsilon\sigma^n \rho^{n/3}/k_{\text{B}}T$$

One can show that this is always positive. The explicit occurrence of the factor T^{-1} in this expression for α reflects the fact that thermal expansion as conventionally defined is not dimensionless.

The fact that Φ_o for this model is homogeneous of degree minus- n produces important simplifications for inherent structures and their energies. Let configuration $\mathbf{r}_1^{(a)} \dots \mathbf{r}_N^{(a)}$ represent a minimum of Φ_o under the condition that volume is fixed at V_a . Then as the volume is changed to some other value V_b the isochoric inherent structure scales continuously to

$$\mathbf{r}_1^{(b)} \dots \mathbf{r}_N^{(b)} = (V_b/V_a)^{1/3} \mathbf{r}_1^{(a)} \dots (V_b/V_a)^{1/3} \mathbf{r}_N^{(a)} \quad (3.5)$$

At the same time the isochoric inherent structure potential energy changes from $\Phi_o^{(a)}$ to

$$\Phi_o^{(b)} = (V_a/V_b)^{n/3} \Phi_o^{(a)} \quad (3.6)$$

The persistence (with scaling) of each isochoric inherent structure implies that under isobaric (constant p) conditions the same inherent structures also appear, though each would have its own characteristic volume. Specifically, the potential enthalpy function Ψ for inherent structure l is determined by minimizing

$$V^{-n/3} \Phi_o^{(l)}(V_a) + pV \quad (3.7)$$

leading to the result

$$\begin{aligned} \Psi^{(l)}(p) &= \left(\frac{3}{n}\right)^{(n-3)/(n+3)} p^{n/(n+3)} [\Phi_o^{(l)}(V_a)]^{3/(n+3)} \\ V^{(l)}(p) &= [n\Phi_o^{(l)}(V_a)/3p]^{3/(n+3)} \end{aligned} \quad (3.8)$$

Numerical simulations of inverse-power systems at fixed volume reveal that the isochoric inherent structures obtained from the liquid state are very narrowly distributed in energy, and that this narrow distribution is essentially temperature-independent. The basic scaling property indicates that the distribution of pressures for the inherent structure must similarly be very narrowly distributed, and so the same must be true for the enthalpy quantities $\Psi^{(l)}$. Equation 3.8 thus requires that $V^{(l)}(p)$ will also be narrowly distributed and independent of liquid temperature.

Returning to eq 2.13, these considerations indicate that for the inverse power model liquid, temperature change causes virtually no shift in basin population: the second sum in eq 2.13 essentially vanishes. This is reasonable in view of the fact that the relative size of all basins, and their relative ordering in energy, pressure, and enthalpy are all unchanged by volume variations. The temperature variation of the pair correlation function is then strictly an intra-basin vibrational phenomenon. Thus for both the crystal and fluid phases

$$\alpha \cong \alpha_{\text{vib}} \quad (3.9)$$

though the numerical values may differ for the two phases.

B. Hard Sphere Model. The virial equation of state for hard spheres of diameter σ takes the following form:¹⁰

$$\frac{p}{\rho k_{\text{B}}T} = 1 + \frac{2}{3} \pi \rho \sigma^3 g^{(2)}(\sigma, \rho) \quad (3.10)$$

which involves the temperature-independent pair correlation function evaluated at the contact distance σ . Differentiation leads to an expression for this system's thermal expansion coefficient:

$$\alpha = \left\{ \frac{1 + (2/3)\pi\rho^3 g^{(2)}(\sigma, \rho)}{1 + (2/3)\pi\sigma^3 \frac{\partial}{\partial \rho} [\rho g^2(\sigma, \rho)]} \right\} \frac{1}{T} \quad (3.11)$$

The quantity enclosed in curly brackets in this last expression is a function only of the reduced density variable $\rho\sigma^3$, and because it is always positive, so too is α . The superficial similarity between α expressions 3.4 and 3.11 is hardly surprising, considering that the hard sphere pair potential

emerges from the $n \rightarrow +\infty$ limit of the inverse power pair potential:^{9,18}

$$\lim_{n \rightarrow +\infty} \epsilon(\sigma/r)^n = +\infty \quad (r < \sigma)$$

$$= 0 \quad (r > \sigma) \quad (3.12)$$

The interparticle potential energy Φ_o in the hard-sphere limit collapses to zero for any physically realizable configuration. It is known that isochoric inherent structures in this limit geometrically correspond to sphere packings, where the individual particles are positioned as though they had diameters sufficiently larger than σ to be spatially jammed.¹⁸ However, under positive-pressure isobaric conditions the resulting inherent structures are just the jammed configurations of the σ -diameter spheres themselves. The volumes $V^{(l)}$, of course, are independent of p , have a minimum for regular crystalline close packing, and exhibit a range of larger values for more disordered sphere packings. The potential enthalpies thus are simply

$$\Psi^{(l)}(p) = pV^{(l)} \quad (3.13)$$

Because the hard sphere model connects to the inverse power model through the large- n limit, eq 3.12, we can conclude that eq 3.9 is also valid for hard spheres.

C. Gaussian Core Model. The third specific case for consideration involves additive pair interactions that are Gaussian functions of distance:

$$v(r) = \epsilon \exp(-r^2/\sigma^2) \quad (3.14)$$

This choice produces several special mathematical features that are not shared by other models.¹¹ Furthermore, a substantial simulational database now exists for this Gaussian core model,^{11,19–21} which may afford an idealized view of some micellar and polymer solutions.

The attribute of the Gaussian core model that is most significant for the present study is that it exhibits a negative- α region of its phase plane that encompasses both BCC crystal and fluid phases.¹¹ For illustrative purposes we focus on the behavior of the model at reduced density

$$\rho^* \equiv \rho\sigma^3 = 0.7 \quad (3.15)$$

at which the BCC crystal has a melting point at the reduced temperature

$$T_{\text{mp}}^*(0.7) \equiv k_{\text{B}}T_{\text{mp}}(0.7)/\epsilon = 0.00197 \quad (3.16)$$

As temperature increases from absolute zero, through T_{mp}^* , and into the stable fluid range, the pressure declines monotonically until it passes through a minimum at

$$T_{\text{min}}^*(0.7) = 0.0183 \quad (3.17)$$

Pressure rises monotonically with temperature beyond this minimum.

The general thermodynamic identity

$$\alpha = \kappa_{\text{T}} \left(\frac{\partial p}{\partial T} \right)_{\rho} \quad (3.18)$$

where κ_{T} is the isothermal compressibility (never negative), requires obviously that α have the same sign as the isochoric temperature derivative of pressure. Consequently, $T_{\text{min}}^*(\rho^*)$ for the Gaussian core model is the locus in the ρ^* , T^* plane across which α changes sign. Equivalently, it is the locus of density

maxima for the system examined at constant pressure. Numerical simulations for the Gaussian core model indicate that $T_{\text{min}}^*(\rho^*)$ is a properly defined positive function of ρ^* for all

$$0.30 \lesssim \rho^* \quad (3.19)$$

although it appears to converge to zero as ρ^* increases to infinity.¹¹

It is important to point out that even in the limit of absolute zero temperature, with ρ^* in the range (3.19), α remains negative. As an example, one finds at $\rho^* = 0.7$, $T^* = 0$:

$$\alpha^* = \epsilon\alpha/k_{\text{B}} \cong -0.437 \quad (3.20)$$

The significance of this result is that it must be a purely intra-basin vibrational phenomenon. In this low temperature limit, the system resides exclusively in one of the permutation-equivalent basins for the perfect BCC crystal.

While the isochoric inherent structures for the fluid phase above $T_{\text{mp}}^*(0.7)$ are not all identical, they are statistically similar to one another and are very narrowly distributed in energy, an attribute that also occurs at other densities. The same narrowness of distribution is also expected when the inherent structures are obtained by isobaric quenching. As a result we must again conclude that the fluid-phase α in both its negative and positive regimes is essentially an anharmonic intra-basin phenomenon.

The appearance of negative thermal expansion in the Gaussian core model can be attributed to unusual mathematical properties displayed by its interaction potential energy Φ_o and associated potential enthalpy Ψ . To be specific, decreasing the volume for a fixed number N of particles causes the topography of the multidimensional Φ_o hypersurface to become smoother.¹¹ This causes a reduction in the number of local minima (isochoric inherent structures), although the BCC crystal and at least some of the amorphous structures survive the reduction. Furthermore, the difference in energy between the surviving inherent structures, as well as the saddle points that connect their basins, declines as volume decreases. Consequently, the relevant basins flare outward, flatten, and act in a less confining manner under compression. This is just the opposite of the usual behavior, wherein compression tends to increase particle confinement. When a temperature rise induces the Gaussian core system to seek a condition of lesser confinement (i.e., higher configurational entropy), it contracts.

The occurrence of a negative α can also be explained²² by noting that the mathematical form of $v(r)$ given in eq 3.14 leads to negative curvature for $r/\sigma < 2^{-1/2}$. This means that the repulsive force between two particles diminishes as their mutual separation decreases below $2^{-1/2}\sigma$. These close encounters are more and more frequent as temperature rises, resulting in a net reduction in interparticle repulsive forces. Hence, at high enough density, the pressure decreases with increased temperature.

Although thermal expansion in the three models just examined arises almost exclusively from intra-basin vibrational effects, important examples exist wherein interbasin equilibration apparently plays a dominating role. In particular, this latter behavior arises in many good glass-forming liquids. As such substances are isobarically supercooled across and below their glass transition temperatures T_{g} , α typically experiences a large reduction, often by a factor of 2 or more.²³ The glass transition marks the point below which configuration (interbasin) relaxation experiences kinetic arrest, with the consequence that $\alpha_{\text{vib}} + \alpha_{\text{str}}$ for these substances suddenly reduces to α_{vib} alone. In contrast to the three simple models discussed above, glass-forming systems exhibit mean inherent structure energies and

enthalpies that depend on the temperature of the liquid; this attribute has been demonstrated both for the model system composed of a two-component Lennard–Jones particle mixture,²⁴ as well as for the real system *o*-terphenyl.¹⁵

IV. Classical Generalizations

The case of materials composed of polyatomic molecules requires an extension of the formalism presented in Section II. The configuration of each molecule *i* now may be specified by the following direct-sum vectors:

$$\mathbf{t}_i = \mathbf{r}_i \oplus \mathbf{s}_i \quad (4.1)$$

The 3-component vector \mathbf{r}_i has the same interpretation as before, the centroid position of molecule *i*. Internal degrees of freedom (orientation, dihedral angles of rotation about bonds, bond length changes) are comprised in \mathbf{s}_i , the number of components of which may vary between species. At the level of pairwise additivity for intermolecular interactions, the potential energy Φ_0 now must be extended to the following format:

$$\Phi_0 = \sum_{i=1}^N v_\gamma^{(1)}(\mathbf{s}_i) + \sum_{i=2}^N \sum_{j=1}^{i-1} v_{\gamma\delta}^{(2)}(\mathbf{t}_i, \mathbf{t}_j) \quad (4.2)$$

a straightforward generalization of the earlier eq 2.6. As before, the Greek subscripts γ and δ denote the chemical species of molecules *i* and *j*, respectively. The $v_\gamma^{(1)}$ represent the intramolecular potential energy functions for each of the species present.

The virial eq 2.5 continues to hold in this polyatomic generalization, where \mathbf{F}_{oi} is the net force on molecule *i* due to all others with which it interacts. Formally we have

$$\mathbf{F}_{oi} = -\nabla_i \Phi_0 \quad (4.3)$$

where the gradient operator ∇_i involves differentiation only with respect to the three components of the centroid position \mathbf{r}_i . The intramolecular potentials $v_\gamma^{(1)}$ do not contribute directly to this net force because they depend only on the internal degrees of freedom \mathbf{s}_i .

Transforming virial expression eq 2.5 to a form that reveals its dependence on molecular short-range order requires first defining polyatomic pair correlation functions. Specifically we write $\rho_\gamma \rho_\delta g_{\gamma\delta}^{(2)}(\mathbf{t}_i, \mathbf{t}_j)$ for the pair distribution function of γ , δ molecular pairs in the given molecular configurations. With appropriate boundary conditions these distribution functions can be invariant to translations and overall rotations, for both fluid and crystalline phases. In the event that the system is in an isotropic amorphous phase, we have for an infinite system the normalization:

$$\lim_{r_{ij} \rightarrow \infty} \int d\mathbf{s}_i \int d\mathbf{s}_j g_{\gamma\delta}^{(2)}(\mathbf{t}_i, \mathbf{t}_j) = 1 \quad (4.4)$$

With this definition in hand, we can now present the polyatomic extension of eq 2.7.

$$p = \rho k_B T - (\rho^2/6) \sum_{\gamma, \delta=1}^v x_\gamma x_\delta \int d\mathbf{r}_{12} \int d\mathbf{s}_1 \int d\mathbf{s}_2 \times \\ [\mathbf{r}_{12} \cdot \nabla_{12} v_{\gamma\delta}^{(2)}(\mathbf{t}_1, \mathbf{t}_2)] g_{\gamma\delta}^{(2)}(\mathbf{t}_1, \mathbf{t}_2) \quad (4.5)$$

Consistent with the earlier usage, ρ stands for the total molecular number density, and the x_γ are species mole fractions. It is worth

stressing that intramolecular forces make no direct contribution to the pressure.

Inherent structures for polyatomic substances are mechanically stable arrangements of molecules that represent a balance of intramolecular, intermolecular, and wall forces. They emerge from the generalization of the isobaric mapping differential equations (2.11) to include the intramolecular degrees of freedom ($s \geq 0$):

$$d\mathbf{t}_i(s)/ds = -\nabla_{\mathbf{t}_i} \Psi[\mathbf{t}_1(s) \dots V(s)] \\ dV(s)/ds = -\partial \Psi[\mathbf{t}_1(s) \dots V(s)] / \partial V \quad (4.6)$$

where now the gradient operator covers all components of \mathbf{t}_i . This mapping again partitions the system's configuration space into basins of attraction surrounding the configuration of each inherent structure. The dimension of that configuration space has now expanded from $3N$ to:

$$3N + \sum_{\gamma=1}^v N_\gamma u_\gamma \quad (4.7)$$

where u_γ is the number of internal degrees of freedom for molecular species γ (i.e. the number of components of the corresponding \mathbf{s}_i).

With the basin division of the configuration space in hand, we can now, in principle, resolve each pair correlation function into separate contributions from each basin *l*. Hence the prior eq 2.12 trivially extends to the following:

$$g_{\gamma\delta}^{(2)}(\mathbf{t}_1, \mathbf{t}_2) = \sum_l P_l(T, p) g_{\gamma\delta}^{(2)}(\mathbf{t}_1, \mathbf{t}_2) \quad (4.8)$$

where P_l is the residency probability for basin *l*. This in turn leads to the generalization of eq 2.13:

$$[\partial g_{\gamma\delta}^{(2)}(\mathbf{t}_1, \mathbf{t}_2) / \partial T]_p = \sum_l P_l [\partial g_{\gamma\delta}^{(2)}(\mathbf{t}_1, \mathbf{t}_2) / \partial T]_p + \\ \sum_l (\partial P_l / \partial T)_p g_{\gamma\delta}^{(2)}(\mathbf{t}_1, \mathbf{t}_2) \quad (4.9)$$

The two sums in the right member of this last equation represent intra-basin vibrational and interbasin structural contributions, respectively. Differentiating the pressure equation of state (eq 4.5) and rearranging the result leads to the polyatomic extension of the simple eq 2.9 for α :

$$\alpha = (2p - \rho k_B T)^{-1} \{ \rho k_B - \\ (\rho^2/6) \sum_{\gamma, \delta=1}^v x_\gamma x_\delta \int d\mathbf{r}_{12} \int d\mathbf{s}_1 \int d\mathbf{s}_2 \times \\ [\mathbf{r}_{12} \cdot \nabla_{12} v_{\gamma\delta}^{(2)}(\mathbf{t}_1, \mathbf{t}_2)] [\partial g_{\gamma\delta}^{(2)}(\mathbf{t}_1, \mathbf{t}_2) / \partial T]_p \} \quad (4.10)$$

Finally, inserting the separated form (eq 4.9) for the pair correlation temperature derivatives once again effects a separation of α into a purely intra-basin vibrational part (eq 4.10 with just the first sum from eq 4.9), plus a structural equilibration correction. Equation 2.14 still applies.

The other direction of generalization to be considered is that associated with nonpairwise-additive molecular interactions. These can be significant when ionic or highly polar species are present, creating large local electric fields with associated electronic polarization effects. They can also be expected if the chemical species that are present exhibit formation and dissociation of chemical bonds. In this circumstance we must now

use the following general format for the total molecular potential function:

$$\Phi_o = \sum_{i=1}^N v_{\gamma}^{(1)}(\mathbf{s}_i) + \sum_{n=2}^{\infty} \sum_{i_1 < \dots < i_n} v_{\gamma \dots \omega}^{(n)}(\mathbf{t}_{i_1} \dots \mathbf{t}_{i_n}) \quad (4.11)$$

For most applications of interest, it seems reasonable to suppose that this is a rapidly converging sum, and that large n values need not be considered.

The forces \mathbf{F}_{oi} that appear in the virial relation (eq 2.5) now receive contributions from all nonvanishing $v^{(n)}$, $n > 1$. This leads in turn to an expression for p that incorporates molecular correlation functions $g^{(n)}$ of comparable orders:

$$p = \rho k_B T - (1/3) \sum_{n=2}^{\infty} (\rho^n/n!) \sum_{\gamma \dots \omega} x_{\gamma \dots \omega} \int d\mathbf{s}_1 \int d\mathbf{t}_2 \dots \int d\mathbf{t}_n \times \\ \left[\left(\sum_{i=1}^n \mathbf{r}_i \cdot \nabla_i \right) v_{\gamma \dots \omega}^{(n)}(\mathbf{t}_1 \dots \mathbf{t}_n) \right] g_{\gamma \dots \omega}^{(n)}(\mathbf{t}_1 \dots \mathbf{t}_n) \quad (4.12)$$

The n th order correlation functions introduced here are subject to normalization conditions analogous to those shown in eq 4.4, namely reduction to unity when all pair distances become large, and upon integration over the internal degrees of freedom $\mathbf{s}_1 \dots \mathbf{s}_n$.

By applying the differential operator $(\partial/\partial T)_p$ to both sides of the general eq 4.12, and then rearranging results, the following expression for α emerges:

$$\alpha = D^{-1} \left\{ \rho k_B - \frac{1}{3} \sum_{n=2}^{\infty} \frac{\rho^n}{2n!} \sum_{\gamma \dots \omega} x_{\gamma \dots \omega} \int d\mathbf{s}_1 \int d\mathbf{t}_2 \dots \int d\mathbf{t}_n \times \right. \\ \left. \left[\left(\sum_{i=1}^n \mathbf{r}_i \cdot \nabla_i \right) v_{\gamma \dots \omega}^{(n)}(\mathbf{t}_1 \dots \mathbf{t}_n) \right] \left[\frac{\partial g_{\gamma \dots \omega}^{(n)}(\mathbf{t}_1 \dots \mathbf{t}_n)}{\partial T} \right]_p \right\} \quad (4.13)$$

The denominator D previously could be expressed entirely in terms of thermodynamic quantities (Eqs 2.9, 4.10), but now includes explicit molecular corrections from $n > 2$ interactions:

$$D = 2p - \rho k_B T - \\ \frac{1}{3} \sum_{n=3}^{\infty} \frac{(n-2)\rho^n}{n!} \sum_{\gamma \dots \omega} x_{\gamma \dots \omega} \int d\mathbf{s}_1 \int d\mathbf{t}_2 \dots \int d\mathbf{t}_n \times \\ \left[\left(\sum_{i=1}^n \mathbf{r}_i \cdot \nabla_i \right) v_{\gamma \dots \omega}^{(n)}(\mathbf{t}_1 \dots \mathbf{t}_n) \right] g_{\gamma \dots \omega}^{(n)}(\mathbf{t}_1 \dots \mathbf{t}_n) \quad (4.14)$$

Despite the extra complexity, expression (4.13) for α displays the same property as before that permits separation into vibrational and structural equilibration components. Each correlation function temperature derivative can be resolved [as in eq 4.9 above for $n = 2$] into distinct intra-basin and interbasin contributions, and so α_{vib} and α_{str} in eq 2.14 continue in principle to be well defined.

V. Quantum Statistics

The classical statistical analysis that has dominated the discussion thus far becomes inappropriate if the system's constituent particles contain light atoms and/or possess high-frequency intramolecular vibrations. In particular, the presence of hydrogen or deuterium can be an aggravating circumstance. For some limited applications it may be acceptable to disregard intramolecular vibrational degrees of freedom and to postulate an "effective" interaction potential for use in classical statistical

mechanics that implicitly incorporates residual quantum effects. Nevertheless, it is important to understand the deeper quantum statistical mechanical context and how it affects thermal expansion.

Diagonal elements of the density matrix, in the position representation, play the role for quantum statistics that has been assigned to the classical configuration distribution function.²⁵ Integrating this diagonal density matrix over each of the Ψ basins in turn generates the quantum versions of the basin residence probabilities $P_i(T)$ that have been central to the preceding analysis. The basins and inherent structures themselves depend only on the given potential enthalpy function Ψ , and do not depend on the subsequent applicability of classical versus quantum statistics. However the $P_i(T)$ do reflect the influence of spin, statistics, energy level quantization, and tunneling effects.

The virial equation of state for quantum systems can be put into a form that is outwardly similar to the classical version. Mazo and Kirkwood²⁶ have shown, for the case of a single spherically symmetric species, that the virial expression for the pressure takes the form:

$$p = \rho k_B \tau(\rho, T) - (2\pi\rho^2/3) \int_0^{\infty} r^3 [\partial v^{(2)}(r)/\partial r] g^{(2)}(r) dr \quad (5.1)$$

Here τ is an effective temperature equal to two-thirds of the mean kinetic energy per particle, divided by k_B . Quantum zero-point motions increase τ above T .

By applying the usual differential operators $(\partial/\partial T)_p$ to both sides of eq 5.1, followed by rearrangement to produce an expression for α , two types of terms are encountered, just as before. The collection of terms that include the P_i , but not their temperature derivatives should be identified as the intra-basin vibrational quantity α_{vib} . The remainder, containing the $(\partial P_i/\partial T)_p$, comprises the structural equilibration portion of thermal expansion, and as before would be designated by α_{str} . Both α_{vib} and α_{str} would manifest the effects of quantization.

As noted earlier, low temperature crystals are essentially confined configurationally to one of the permutationally equivalent basins for the absolute Ψ minimum. Motions about this minimum are resolvable in terms of phonon excitations. Anharmonicity is conventionally described as volume dependence of phonon frequencies, or more compactly as a volume dependence of the crystal Debye temperature $\Theta(V)$, often expressed as the Grüneisen constant²⁷

$$\Gamma = -d \ln \Theta / d \ln V \quad (5.2)$$

This in turn can be converted to α_{vib} , the only contribution to crystal thermal expansion.

VI. Density Maximum in Water

Understanding thermal expansion effects in the condensed phases of water presents an unusual challenge. The substance evokes each of the generalizations discussed above: (a) it is composed of polyatomic molecules with internal rotational and vibrational degrees of freedom; (b) intermolecular interactions include at least three-molecule contributions with significant magnitudes but variable sign;^{28,29} and (c) the presence of two hydrogen atoms in each molecule produces substantial quantum effects at room temperature and below. This Section VI is devoted to one modest aspect of the pure water problem, namely a rough analysis of how the famous liquid-phase density maximum at 4 °C is determined by a balance between vibrational and structural equilibration influences.

The ambient-pressure inherent structures for water that possess the lowest potential enthalpy values are those that correspond to the structure of ice Ih and the closely related ice Ic. These crystals exhibit 4-fold coordination for each water molecule to nearest neighbors by hydrogen bonding. The structures are not unique, because the pattern of hydrogen bonds can be fulfilled in many ways that differ only in orientation of the participating water molecules. The number of distinct ice inherent structures for an N -molecule crystal is close to the Pauling estimate:^{30,31}

$$(3/2)^N \quad (6.1)$$

These alternatives appear to be nearly degenerate in potential enthalpy, and to give rise to the calorimetrically measured residual entropy of ice at absolute zero.³²

The thermal expansion of ice Ih is negative below about 65 K, but changes sign upon heating.^{1,33} In the vicinity of its melting point, one finds¹

$$\alpha(\text{Ih}) \cong (54 + 0.24t) \times 10^{-6}/\text{deg} \quad (6.2)$$

where t is the Celsius temperature. Evidently this is a purely intra-basin vibrational phenomenon, because virtually all of the relevant ice Ih basins have nearly equal a priori occupation probabilities. The specific result (eq 6.2) represents a combination of effects from the attributes (a), (b), and (c) mentioned above.

The melting of ice to produce liquid water deforms and breaks hydrogen bonds. The extent of this structural damage can be gauged by comparing the cohesive energies of ice Ih and of liquid water at 0 °C:³⁴

$$\begin{aligned} \text{ice Ih: } & 11.661 \text{ kcal/mol} \\ \text{liquid: } & 10.225 \text{ kcal/mol} \end{aligned} \quad (6.3)$$

On account of the weaker binding present in the liquid, we can reasonably expect that its inherent structures will produce an intra-basin vibrational component α_{vib} to the total thermal expansion of the liquid that exceeds the ice Ih result shown in (eq 6.2) above. We propose that a crude estimate of this enhancement can be based on the intuitive notion that weaker molecular binding entails correspondingly smaller force constants, larger vibrational amplitudes, and thus increased anharmonicity. For this reason, we choose to scale-up $\alpha(\text{Ih})$, eq 6.2, by the ratio of cohesive energies, eq 6.3:

$$\begin{aligned} \alpha_{\text{vib}}(\text{liq}, t) & \cong 1.14\alpha(\text{Ih}) \\ & \cong (61.6 + 0.274t) \times 10^{-6}/\text{deg} \end{aligned} \quad (6.4)$$

We can now address the issue of how the vibrational contribution influences the position of the liquid's density maximum at 4 °C. In this temperature range, the measured thermal expansion coefficient for liquid water can be represented as³⁵

$$\alpha(\text{liq}, t) \cong (-68.1 + 17.1t) \times 10^{-6}/\text{deg} \quad (6.5)$$

Subtracting estimate 6.4 for α_{vib} leaves

$$\alpha_{\text{str}}(\text{liq}, t) \cong (-129.7 + 16.8t) \times 10^{-6}/\text{deg} \quad (6.6)$$

This passes through zero at

$$t = 7.72 \text{ }^\circ\text{C} \quad (6.7)$$

indicating an upward shift in temperature for the purely structural equilibration density maximum by about 3.7 °C.

Admittedly, results 6.6 and 6.7 rely upon the crude and tentative estimate 6.4 for their validity. But even if these results are only qualitatively valid, they raise a significant novel issue concerning the liquid water density maximum. The clear implication is that within structural equilibration by itself, two distinct and competing phenomena are at work. One, which dominates at low temperature (particularly in the supercooled regime), involves a tendency toward more and more open but well-bonded water networks as illustrated by the family of clathrate networks.³⁶ The second, increasing in effect as temperature rises, apparently concerns formation of low-density, fissure-containing inherent structures³⁷ made possible by disruption of a significant fraction of the hydrogen bonds. Both of these phenomena act to lower density, but as temperature rises from supercooling toward boiling, the first weakens before the second fully takes hold, to produce by default a density maximum in the purely structural part of the statistical description. The anharmonic vibrations within basins then act to shift the maximum to the lower observed temperature.

The rationale just presented is speculative at present. However, it is subject to verification or contradiction by a combination of thermal expansion measurements on a variety of water-containing materials of fixed structures but variable extents of hydrogen bonding, and by suitable computer simulation on water models. The density maximum issue, furthermore, is not restricted to ambient pressure, but deserves study both under elevated pressure and in the regime of negative pressures (states of tension).³⁸ The latter may bear on the controversial nature of low-temperature amorphous water.^{39–41}

VII. Discussion

No general examination of thermal expansion would be complete without mentioning its divergent behavior in the liquid–vapor critical region. Even the venerable van der Waals equation of state qualitatively captures this phenomenon. It leads to the following expression for α (where p_c , T_c , and v_c are the critical-point values of pressure, temperature, and molar volume):

$$\alpha = \frac{1}{3T_c} \left(3 - \frac{v_c}{v} \right) \left[\frac{T}{T_c} - \frac{1}{4} \left(\frac{v_c}{v} \right) \left(3 - \frac{v_c}{v} \right)^2 \right] \quad (7.1)$$

Above the critical temperature, along the critical isochore ($v = v_c$), this becomes

$$\alpha = \frac{2}{3T_c} \left(\frac{T}{T_c} - 1 \right) \quad (7.2)$$

while along the critical isotherm ($T = T_c$) it predicts

$$\alpha = \frac{4}{3T_c} \left(3 - \frac{v_c}{v} \right) \left[\left(4 - \frac{v_c}{v} \right) \left(3 - \frac{v_c}{v} \right)^2 \right] \quad (7.3)$$

A more realistic nonclassical description of the liquid–vapor critical region⁴² would replace the divergence exponents 1 and 2 in eqs 7.1 and 7.2 with the Ising universality-class exponents, approximately 1.3 and 3.3, respectively.

The present analysis raises the question of how the critical divergence of α should be apportioned between vibrational and structural equilibration contributions. For the moment this must remain an intriguing open issue. In seeking answers in the future it may be helpful to use computer simulation on simple models

(such as the Lennard-Jones fluid) in the general vicinity of the critical region to characterize their inherent structures and their basins. On account of the divergence of the correlation length at the critical point,⁴² such simulations must necessarily involve large system sizes (large N), and can only approach the true critical point.

A recent study of ZrW_2O_8 suggests that a close connection exists between negative thermal expansion in the crystal phases of framework solids, and the capacity for those solids to undergo pressure-induced amorphization.⁴³ In particular, the negative thermal expansion of ZrW_2O_8 over a wide temperature range at ambient pressure is purely vibrational in origin, arising from low-frequency "rigid unit modes" that substantially preserve the geometries of ZrO_6 and WO_4 polyhedral units. Application of high pressure (>1.5 GPa), however, causes segregation of distinct large-amplitude framework distortions as their own inherent structures. These appear to involve disruption of the low-pressure polyhedral units, leading to the possibility of recovering amorphous ZrW_2O_8 at low pressure and room temperature. Other materials with framework crystal structures and at least some temperature range of negative α (SiO_2, H_2O) can also be amorphized under pressure.

Experience with the theoretical Gaussian core model discussed in Section IIIc above suggests that a negative volume of melting (which it exhibits¹¹) may also be a good indicator of susceptibility to pressure-induced amorphization. The BCC crystal exhibited by this system can, at positive temperature, always be crushed into an amorphous "fluid" state, but this model cannot be described as a framework system. In addition to the previously mentioned real substances, such a criterion suggests that the elements Sb, Bi, and Ga that display negative melting volumes might show pressure-induced amorphization.⁴⁴ More generally, the relationship between negative α and negative volume of melting remains to be explored.

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