Thermodynamics of strongly correlating liquids

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We show that for any strongly correlating liquid, i.e., a liquid with strong correlation between virial and potential energy equilibrium fluctuations in the NVT ensemble, the temperature is product of a function of the excess entropy per particle and a function of density, $T = f(s)g(\rho)$. It follows that the liquid's isomorphs are curves of constant $g(\rho)/T$ and that a Grüneisen type equation of state applies for the configurational degrees of freedom. Some other simple thermodynamic relations valid for strongly correlating liquids are also derived. All relations given are approximate.

I. INTRODUCTION

A series of recent papers by the *Glass and Time* group introduced and discussed the class of strongly correlating liquids and its properties [1, 2]. These liquids are defined by having strong correlations between constant-volume equilibrium fluctuations of virial $W \equiv pV - Nk_BT$ (N is the number of particles) and potential energy U, with a correlation coefficient above 0.9. The WU correlation coefficient varies with state point, but we found from computer simulations that a system has either poor virial potential energy correlations in all of its phase diagram or is strongly correlating at most condensed-phase state points. Most or all van der Waals liquids and metals are strongly correlating. In contrast, hydrogen-bonded liquids, strongly ionic liquids, and covalently bonded liquids are generally not strongly correlating because competing interactions spoil the WU correlation (except presumably at very high pressure [3]). Theoretical arguments and numerical evidence show that strongly correlating liquids are simpler than liquids in general [1]. A recent paper summarizes the most important properties of strongly correlating liquids [4].

The relative simplicity of strongly correlating liquids derive from the fact that these liquids are characterized by having "isomorphs" in their phase diagram [1, 2], which are the equivalence classes of the following equivalence relation. Two state points with density and temperature (ρ_1, T_1) and (ρ_2, T_2) are *isomorphic* if all pairs of "physically relevant" microconfigurations [2] with one from each state point, which trivially scale into one another $[\rho_1^{1/3}\mathbf{r}_i^{(1)} = \rho_2^{1/3}\mathbf{r}_i^{(2)}]$, have proportional configurational Boltzmann factors:

$$e^{-U(\mathbf{r}_1^{(1)},...,\mathbf{r}_N^{(1)})/k_BT_1} = C_{12}\, e^{-U(\mathbf{r}_1^{(2)},...,\mathbf{r}_N^{(2)})/k_BT_2} . \quad (1)$$

It is understood that the proportionality constant C_{12} is independent of the microconfigurations. Only inverse-power law (IPL) liquids have exact isomorphs, but it has been shown that a liquid is strongly correlating if and

only if it to a good approximation has isomorphs (Appendix A of Ref. 2). In Ref. 2 it was further shown that this happens if and only if the constant potential energy surface in R^{3N} is invariant along isomorphs; this geometric characterization, which recently led us to introduce "NVU dynamics" [5], plays no role below, however.

The invariance along an isomorph of the canonical probabilities of scaled configurations has several implications [1, 2]: The excess entropy is isomorph invariant and so is the isochoric specific heat; the reduced-unit dynamics is invariant for both Newtonian and stochastic dynamics; all reduced-unit static correlation functions, e.g., the pair correlation function $g(r)$, are isomorph invariant. It is important to emphasize that, since the isomorph concept is approximate (except for IPL systems), isomorph invariants are also approximate. Likewise, the thermodynamic relations derived below are also generally approximate. All isomorph invariants are exact invariants for IPL systems, but not all IPL isomorph invariants give rise to general (approximate) isomorph invariants: Only IPL isomorph invariants like entropy, dynamics, etc, which are independent of the value of the constant C_{12} (which is unity in IPL systems) give rise to general isomorph invariants [1, 2, 4].

This note focuses on the thermodynamics of strongly correlating liquids, starting from the isomorph invariance of excess entropy and isochoric specific heat. Below, all thermodynamic quantities are excess quantities, i.e., in excess of those of an ideal gas at the same density and temperature. Thus S is the excess entropy (a quantity that is negative because the liquid has more order than an ideal gas at same density and temperature), C_V is the excess isochoric specific heat, U is the potential energy, i.e., the excess energy, p is henceforth the excess pressure, i.e., $p = W/V$, $\beta_V \equiv (\partial p/\partial T)_V$ is the pressure coefficient of the excess pressure, etc. Small letters denote intensive quantities, for instance $s \equiv S/N$ and $c_V \equiv C_V/N$.

II. A THERMODYNAMIC SEPARATION RELATION CHARACTERIZING STRONGLY CORRELATING LIQUIDS

As mentioned, both the isochoric specific heat C_V and the entropy S are invariant along an isomorph. The proof

of this is staightforward [2]: The entropy is determined by the canonical probabilities, and since these are identical for scaled microconfigurations of two isomorphic state points, entropy is an isomorph invariant. According to Einstein's formula one has $C_V = \langle(\Delta U)^2\rangle/k_B T^2$, from which C_V is easily proved to be an isomorph invariant by utilizing the logarithm of Eq. (1).

That S and C_V are invariant along the same curves in the phase diagram implies that C_V is a function of S:

$$C_V = \phi(S). \tag{2}$$

Thus one has $T(\partial S/\partial T)_V = \phi(S)$, or at constant volume:

$$\frac{dS}{\phi(S)} = \frac{dT}{T}. \tag{3}$$

Integrating this leads to an expression of the form $F(S) = \ln(T) + k(V)$, which implies $T = \exp[F(S)]\exp[-k(V)]$ or

$$T = f(S)h(V) = f(S)g(\rho). \tag{4}$$

The generic version of this involves only intensive quantities $s = S/N$:

$$T = f(s)g(\rho). \tag{5}$$

This is the fundamental separation identity valid for all systems with good isomorphs. For more convenient reference to standard thermodynamics we use below, however, the version Eq. (4). We have not been able to prove that Eq. (4) implies a given system is strongly correlating, but find it likely that this is the case.

III. CONSEQUENCES OF THE THERMODYNAMIC SEPARATION RELATION

Equation (4) has several consequences:

1. Equation (4) implies Eq. (2).

2. The variable characterizing an isomorph, Γ, may be chosen as

$$\Gamma = \frac{g(\rho)}{T}. \tag{6}$$

3. The (reduced) relaxation time τ may be written $\tau = G[g(\rho)/T]$ [6].

4. The density-scaling exponent γ is given by

$$\gamma = \frac{d\ln g}{d\ln\rho}. \tag{7}$$

In particular, γ is a function of density only: $\gamma = \gamma(\rho)$.

5. The density-scaling exponent is given by $\gamma = \beta_V/c_V$ where $\beta_V \equiv (\partial p/\partial T)_V$ [2].

6. U has the form

$$U = g(\rho)H(S) + A(\rho) \tag{8}$$
$$= T\phi(S) + A(\rho). \tag{9}$$

7. A Grüneisen-type equation of state applies,

$$W = \gamma(\rho)U + \Phi(\rho). \tag{10}$$

To prove point 1 we differentiate Eq. (4) with respect to temperature at constant volume and use $g(\rho) = T/f(S)$

$$1 = f'(S)\left(\frac{\partial S}{\partial T}\right)_V g(\rho) = f'(S)C_V/f(S). \tag{11}$$

It follows that $C_V = f(S)/f'(S)$ is a function of the entropy. Point 2 follows from Eq. (4) written as $1/f(S) = g(\rho)/T$ combined with the isomorph invariance of entropy. Point 3 follows from the isomorph invariance of τ. To derive points 4 and 5, recall the definition of the density-scaling exponent [1, 2]

$$\gamma = \left(\frac{\partial\ln T}{\partial\ln\rho}\right)_\tau = \left(\frac{\partial\ln T}{\partial\ln\rho}\right)_S. \tag{12}$$

Equation (4) implies $d\ln T = d\ln f(S) + d\ln g(\rho)$. Thus along an isomorph one has $d\ln T = d\ln g$, which via Eq. (12) implies Eq. (7). In particular, γ is a function of density only: $\gamma = \gamma(\rho)$. In order to derive the thermodynamic expression for γ of point 5 we differentiate Eq. (4) with respect to volume at constant temperature:

$$0 = f'(S)\left(\frac{\partial S}{\partial V}\right)_T h(V) + f(S)h'(V). \tag{13}$$

A Maxwell relation implies $(\partial S/\partial V)_T = (\partial p/\partial T)_V \equiv \beta_V$. Thus, since the isochoric specific heat per unit volume is given by $c_V = f(S)/[f'(S)V]$, i.e., $f'(S) = f(S)/(Vc_V)$, we get

$$0 = \frac{f(S)}{Vc_V}\beta_V h(V) + f(S)h'(V), \tag{14}$$

or

$$\frac{\beta_V}{c_V} = -V\frac{h'(V)}{h(V)} = -\frac{d\ln h}{d\ln V} = \frac{d\ln g}{d\ln\rho} = \gamma. \tag{15}$$

To prove point 6 we note that $(\partial U/\partial T)_V = C_V = \psi(T/g(\rho))$, which by integration leads to Eq. (8). Finally, to derive the Grüneisen equation of state in its

configuration space version we first note that $TdS = dU + pdV = dU - Wd\ln\rho$, i.e.,

$$W = \left(\frac{\partial U}{\partial \ln \rho}\right)_S .\tag{16}$$

Combining this with Eq. (8) leads to

$$
\begin{aligned}
W &= \frac{dg}{d\ln\rho}H(S) + \rho A'(\rho) &\tag{17}\\
&= \frac{dg}{d\ln\rho}\frac{U - A(\rho)}{g(\rho)} + \rho A'(\rho) &\tag{18}\\
&= \frac{d\ln g}{d\ln\rho}[U - A(\rho)] + \rho A'(\rho) &\tag{19}\\
&= \gamma(\rho)U + \Phi(\rho). &\tag{20}
\end{aligned}
$$

IV. TWO FURTHER THERMODYNAMIC RELATIONS FOR STRONGLY CORRELATING LIQUIDS

The Helmholtz free energy F has the following form

$$F = Ta(S) + b(V)\tag{21}$$

where a and b are some functions. This result follows from Eq. (8): $F = U - TS = T\phi(S) + A(\rho) - TS = T(\phi(S) - S) + A(\rho) = Ta(S) + b(V)$.

The final relation we derive is

$$U = pa(V) + b(V)\tag{22}$$

where again a and b are generic functions (not the same as above). The relation follows directly from the configurational Grüneisen relation Eq. (10) via the definition of the virial.

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