Communication: Thermodynamics of condensed matter with strong pressure-energy correlations

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We show that for any liquid or solid with strong correlation between its NVT virial and potential-energy equilibrium fluctuations, the temperature is a product of a function of excess entropy per particle and a function of density, \( T = f(s) h(\rho) \). This implies that (1) the system’s isomorphs (curves in the phase diagram of invariant structure and dynamics) are described by \( h(\rho)/T = \text{Const.} \), (2) the density-scaling exponent is a function of density only, and (3) a Grüneisen-type equation of state applies for the configurational degrees of freedom. For strongly correlating atomic systems one has \( h(\rho) = \sum_n C_n \rho^{n/3} \) in which the only non-zero terms are those appearing in the pair potential expanded as \( v(r) = \sum_i v_{ii} r^{-n} \). Molecular dynamics simulations of Lennard-Jones type systems confirm the theory. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.3685804]

The class of strongly correlating liquids was introduced in Refs. 1 and 2. These liquids are defined by having a correlation coefficient above 0.9 of the constant-volume equilibrium fluctuations of virial \( W \) and potential energy \( U \). The \( WU \) correlation coefficient varies with state point, but we found from computer simulations that a system has either poor \( WU \) correlations in the entire phase diagram or is strongly correlating at most of its condensed-phase state points.1–5 Van der Waals and metallic liquids are generally strongly correlating, whereas hydrogen-bonded, ionic, and covalently bonded liquids are generally not. The solid phase is usually at least as strongly correlating as the liquid phase. Theoretical arguments, numerical evidence, and experiments show that strongly correlating liquids are simpler than liquids in general.1–7

The simplicity of strongly correlating liquids compared to liquids in general8 derives from the fact that the former have “isomorphs” in their phase diagram, which are curves of isomorphic state points. Two state points with particle density and temperature \((\rho_1, T_1)\) and \((\rho_2, T_2)\) are termed isomorphic if all pairs of physically relevant microconfigurations of the state points that trivially scale into one another (i.e., \( \rho_1^{1/3} \mathbf{r}_i^{(1)} = \rho_2^{1/3} \mathbf{r}_i^{(2)} \) for all particles \( i \)) have proportional configurational Boltzmann factors:

\[
\frac{e^{-U(\mathbf{r}_i^{(1)})/k_B T_1}}{e^{-U(\mathbf{r}_i^{(2)})/k_B T_2}} = C_{12} \frac{e^{-U(\mathbf{r}_i^{(2)})/k_B T_2}}{e^{-U(\mathbf{r}_i^{(1)})/k_B T_1}}.
\]

Only inverse-power-law liquids have exact isomorphs (here \( C_{12} = 1 \)), but as shown in Appendix A of Ref. 3 a system is strongly correlating if and only if it has isomorphs to a good approximation.

The invariance of the canonical probabilities of scaled microconfigurations along an isomorph has several implications, for instance:1–3 (1) the excess entropy and the isochoric specific heat are isomorph invariants, (2) the reduced-unit dynamics is isomorph invariant for both Newtonian and stochastic dynamics, (3) all reduced-unit static correlation functions are isomorph invariant, and (4) a jump between isomorphic state points takes the system instantaneously to equilibrium. Using reduced units means measuring length in terms of the unit \( \rho^{-1/3} \) and time in units of \( \rho^{1/3} \sqrt{m/k_B T} \) where \( m \) is the average particle mass. Since isomorphs are generally approximate, isomorph properties are likewise rarely rigorously obeyed.

All thermodynamic quantities considered below 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 \((S < 0)\), \( C_V \) is the excess isochoric specific heat, \( p \) is the excess pressure (i.e., \( p = W/V \)), etc.

Briefly, the reason that \( S \) and \( C_V \) are isomorph invariants is the following.7 The entropy is determined by the canonical probabilities, which are identical for scaled microconfigurations of two isomorphic state points. From Einstein’s formula \( C_V = (\Delta U^2)/k_B T^2 \) the isomorph invariance of \( C_V \) follows easily by taking the logarithm of Eq. (1) and making use of the isomorph invariance of scaled microconfiguration probabilities.

Since \( S \) and \( C_V \) are invariant along the same curves in the phase diagram, \( C_V \) is a function of \( S \); \( C_V = \phi(S) \). Thus, \( T(\delta S/\delta T)_V = \phi(S) \) or at constant volume: \( dS/\phi(S) = dT/T \). Integrating this leads to an expression of the form \( \psi(S) = \ln(T) + k(V) \), which implies \( T = \exp[-\psi(S)] \exp[-k(V)] \). The generic version of this involves only intensive quantities \((s = S/N)\):

\[
T = f(s) h(\rho).
\]

For inverse-power-law interactions \((\alpha r^{-n})\) the entropy is well known to be a function of \( \rho^{n/3} \) where \( \gamma = n/3 \): \( S = K(\rho^{n/3}) \). Applying the inverse of the function \( K \) shows that these perfectly correlating systems obey Eq. (2) with \( h(\rho) = \rho^{n/3} \).

The thermodynamic separation identity Eq. (2) is the main result of this communication. We proceed to discuss some consequences and numerical tests.

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Density scaling: Since entropy is an isomorph invariant, it follows from Eq. (2) that the variable characterizing an isomorph may be chosen as $h(\rho)/T$. In particular, the reduced relaxation time $\tilde{\tau}$, which is also an isomorph invariant, may be written for some function $G$:

$$\tilde{\tau} = G\left(\frac{h(\rho)}{T}\right).$$

(3)

This is the form of “density scaling" proposed by Albashimionesco et al. in 2004 from different arguments;\textsuperscript{10} at the same time Dreyfus et al., as well as Casalini and Roland, favored the more specific form $\tilde{\tau} = G(\rho^n/T)$.\textsuperscript{10} Isochrones for many supercooled liquids and polymers follow to a good approximation the latter “power-law density scaling" relation.\textsuperscript{11} For large density changes, however, it was recently shown that the density-scaling exponent varies significantly in both simulations and experiments;\textsuperscript{12} these cases conform to the more general equation (3).

An expression for the density-scaling exponent: The general, state-point dependent density-scaling exponent $\gamma$ is defined\textsuperscript{2,3} by

$$\gamma \equiv \left(\frac{\partial \ln T}{\partial \ln \rho}\right)_S = \left(\frac{\partial \ln T}{\partial \ln \rho}\right)_{\tilde{\tau}}. \quad (4)$$

The physical interpretation of Eq. (4) is the following. If density is increased by 1%, temperature should be increased by $\gamma / 100$ for the system to have the same entropy and reduced relaxation time. Equation (2) implies $d \ln T = d \ln f(\rho) + d \ln h(\rho)$; thus alone an isomorph one has $d \ln T = d \ln h$. Via Eq. (4) this implies

$$\gamma = \frac{d \ln h}{d \ln \rho}. \quad (5)$$

In particular, $\gamma$ depends only on density: $\gamma = \gamma(\rho)$.\textsuperscript{3}

**Configurational Grüneisen equation of state:** The Grüneisen equation of state expresses that pressure equals a density-dependent number times energy plus a term that is a function of density only.\textsuperscript{13} This equation of state is used routinely for describing condensed matter at high pressures and temperatures. We proceed to show that strongly correlating systems obey the configurational version of the Grüneisen equation of state, which as suggested by Casalini et al.\textsuperscript{14} has the density-scaling exponent as the proportionality constant:\textsuperscript{3,4}

$$W = \gamma(\rho)U + \Phi(\rho). \quad (6)$$

To prove this, note first that $(\partial U/\partial S)_\rho = T = f(S)h(\rho)$ by integration implies $U = f(S)h(\rho) + k(\rho)$ where $F(S) = f(S)$ ($S$ is the extensive entropy). Since $W = (\partial U/\partial \ln \rho)_S$ (which follows from the standard identity $TdS = dU + pdV$), we get $W = F(S)d\ln \rho + dk/d\ln \rho$. Substituting into the latter expression $F(S)$ isolated from $U = F(S)h(\rho) + k(\rho)$ leads to Eq. (6), in which $\gamma(\rho)$ is given by Eq. (5). It is straightforward to show that, conversely, Eq. (6) implies the thermodynamic separation identity Eq. (2).

The isomorphs of atomic systems: We consider now predictions for systems of “atomic” particles interacting via pair potentials of the form\textsuperscript{15} (where $r$ is the distance between two particles)

$$v(r) = \sum_n v_n r^{-n}. \quad (7)$$

For simplicity only the case of identical particles is considered, but the arguments generalize trivially to multicomponent systems. Consider the thermal average $(r^{-n})$. Switching to reduced units defined\textsuperscript{2,3} by $\tilde{r} \equiv r_0^{1/3}r$, we have $(r^{-n}) = (\tilde{r}^{-n})\rho^{n/3}$. Since structure is isomorph invariant in reduced units, $(\tilde{r}^{-n})$ is an isomorph invariant. Consequently, it is a function of any other isomorph invariant, for instance the entropy: $(\tilde{r}^{-n}) = G_n(S)$. Noting that the average potential energy is a sum of Eq. (7) over all particle pairs, we conclude that (where $H_n(S) \propto _i \nu_i G_n(S)$)

$$U = \sum_n H_n(S)\rho^{n/3}. \quad (8)$$

Taking the derivative of this equation with respect to temperature at constant volume leads to

$$\left(\frac{\partial U}{\partial T}\right)_V = \sum_n H_n(S) \left(\frac{\partial S}{\partial T}\right)_V \rho^{n/3}. \quad (9)$$

The left-hand side is $T(\partial S/\partial T)_V$, so Eq. (9) implies

$$T = \sum_n H_n(S)\rho^{n/3}. \quad (10)$$

This is consistent with the thermodynamic separation identity Eq. (2) only if all the functions $H_n(S)$ are proportional to some function, i.e., if one can write $H_n(S) = C_n \phi(S)$. We identify $\phi(S)$ as the function $f(\rho)$ of Eq. (2), which means that

$$h(\rho) = \sum_n C_n \rho^{n/3}. \quad (11)$$

Thus, for strongly correlating atomic liquids, the thermodynamic function $h(\rho)$ has an analytical structure, which is inherited from $v(r)$ in the sense that the only non-zero terms of $h(\rho)$ are those corresponding to non-zero terms of $v(r)$. Note that not all systems with potentials of Eq. (7) are strongly correlating and that the derivation applies only if this is the case.

As an illustration we present results from NVT simulations of the Kob-Andersen binary Lennard-Jones (KABLJ) liquid,\textsuperscript{16} which is strongly correlating at its condensed-phase state points.\textsuperscript{1–3} The application of the above to LJ systems predicts that $H_{12}(S) \propto H_2(S)$, where $H_{12}(S)$ is the reduced coordinate average of the $r^{-12}$ term of $U$. Integrating this leads to $H_{12}(S) = \alpha H_2(S) + \beta$, implying that if the repulsive term in $U$ is plotted against the attractive term in reduced units, all points are predicted to fall onto a common line. Figure 1 presents data where density was changed by a factor of eight and temperature by a factor of 40 000. The data collapse is good but not exact, which reminds us that the relations derived are approximate.

The theory implies a simple mathematical description of the isomorphs in the $(\rho, T)$ phase diagram. From the fact that the potential energy contains only $r^{-12}$ and $r^{-6}$ terms, it follows that $h(\rho) \propto \rho^4 - 2\rho^2$. Consequently, LJ isomorphs are given by

$$\frac{A\rho^4 - B\rho^2}{T} = \text{Const.} \quad (12)$$
The invariance of the Boltzmann statistical weights of scaled microconfigurations implies that an isomorph cannot cross the liquid-solid coexistence curve. In particular, the coexistence curve is itself predicted to be an isomorph,\(^3\) which was recently confirmed by simulations of generalized LJ liquids.\(^4,17\)

Consequently, the coexistence line is given by Eq. (12). This validates a recent conjecture of Khrapak and Morfill.\(^18\)

Predictions for the repulsive Lennard-Jones fluid. As a final illustration we consider the “repulsive” single-component LJ fluid defined by the pair potential \(\varepsilon_{\text{AA}} = \sigma_{\text{AA}} = 1\). These quantities correspond to \(H_{12}(S)\) and \(H_6(S)\) in Eq. (8). The theory predicts that \(H_{12}(S) \propto H_6(S)\), implying that all data points should fall onto a common line according to \(H_{12}(S) = aH_6(S) + \beta\).

The following. Consider two isomorphic state points (\(\rho_0\), \(T_0\)) and (\(\rho\), \(T\)) and suppose each temperature is changed a little, keeping both densities constant. If the two new state points are also isomorphic, the entropy change is the same for both: \(\Delta U/T_0 = \Delta U/T\). This implies \(\Delta U/\Delta U_0 = T/T_0\), i.e., \((\partial U/\partial U_0)_{\rho, \rho} = T/T_0\). Since \(h(\rho, T)\) is constant along an isomorph, this implies \((\partial U/\partial U_0)_{\rho, \rho} = h(\rho)/h(\rho_0)\). Integrating this at constant \(\rho_0\) and \(\rho\) leads to \(U = [(h(\rho)/h(\rho_0))U_0 + \phi(\rho_0, \rho)]\). In our case of reference density unity \(\rho_0 = 1\) and \(h(\rho_0) = 1\). Thus, plotting \(U\) versus \(U_0\) is predicted to result in straight lines with slope \(h(\rho)\) (yellow asterisks in the left panel of Fig. 2). The scaled state points are isomorphic to the original \(\rho = 1\) state points, with temperatures given by \(T = T_0 h(\rho)\). Via the “direct isomorph check”\(^3\) this implies that the scaled microconfigurations form elongated ovals also with slope \(h(\rho)\).

In summary, we have shown that for strongly correlating liquids or solids, temperature separates into a function of entropy times a function of density. For these systems the energy scale is consequently determined by density alone. It is an open question whether, conversely, the thermodynamic separation identity equation (2) implies that the system in question is strongly correlating. We anticipate that this is the case, at least for realistic potentials.

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