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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 energy per particle and a function of density, $T = f(\rho) h(\rho)$. 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 $h(\rho) = \sum_n C_n \rho^n$ in which the only non-zero terms are those appearing in the pair potential expanded as $v(r) = \sum_i v_i r^{-n}$. Molecular dynamics simulations of Lennard-Jones type systems confirm the theory. © 2012 American Institute of Physics.

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 “isomorphs” in their phase diagram, which are curves of the average particle mass. Since isomorphs are generally approximant, 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.\(^1\) The entropy is determined by the canonical probabilities, which are identical for scaled microconfigurations of two isomorphic state points. From Einstein’s formula $C_V = (\Delta U)^2/k_B T$ 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 ($s \equiv S/N$):

$$T = f(s) h(\rho).$$

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

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

This is the form of “density scaling” proposed by Albashionesco et al. in 2004 from different arguments; at the same time Dreyfus et al., as well as Casalini and Roland, favored the more specific form $\tilde{\tau} = G(\rho^n/T)$.

Grüneisen equation of state expresses that pressure equals reduced relaxation time $\tilde{\tau}$ is an isomorph invariant. Consequently, it is a function of any other isomorph invariant, for instance the entropy: $(\tilde{\tau}^{-n}) = G_n(S)$. Noting that the average potential energy is a sum of Eq. (7) over all particle pairs, we conclude that (where $H_n(S) \propto v_n G_n(S)$)

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

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

$$(\frac{\partial U}{\partial T})_{\tilde{\nu}} = \sum_n H'_n(S)\left(\frac{\partial S}{\partial T}\right)_{\tilde{\nu}} \rho^{n/3}.$$  

The left-hand side is $T(\partial S/\partial T)_{\tilde{\nu}}$, so Eq. (9) implies

$$T = \sum_n H'_n(S)\rho^{n/3}.$$  

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 $H'_n(S) = C_n \phi(S)$.

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

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. 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. has the density-scaling exponent as the proportionality constant:

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

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 $W = F(S)dh/\ln \rho + dk/\ln \rho$. 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 $v(r) = \sum_v v_nr^{-n}$ (where $r$ is the distance between two particles)

$$v(r) = \sum_n v_nr^{-n}.$$  

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 by $\tilde{r} \equiv \rho^{1/3}r$, 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 $H_n(S) \propto v_n G_n(S)$)
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 Krhapak and Mortill.\(^{18}\)

**Predictions for the repulsive Lennard-Jones fluid.** As a final illustration we consider the “repulsive” single-component LJ fluid defined by the pair potential \(v(r) = (r^{-12} + r^{-6})/2\), a system with \(WU/\partial U\) correlation coefficient above 99.9\% in its entire phase diagram. At low densities (\(\rho \ll 1\)) the repulsive LJ fluid behaves as an \(r^{-6}\) fluid, whereas it for \(\rho \gg 1\) is effectively an \(r^{-12}\) fluid. Thus, the density-scaling exponent \(\gamma(\rho)\) varies from 2 to 4 as density increases, a much larger variation than that of previously studied strongly correlating systems.

Since \(h(\rho)\) is only defined within an overall multiplicative constant, one can write for the repulsive LJ fluid \(h(\rho) = \alpha \rho^4 + (1-\alpha)\rho^2\). This leads via Eq. (5) to \(\gamma_0 = 2 + 2\alpha\), where \(\gamma_0\) is the density-scaling exponent at reference density unity, implying that

\[
h(\rho) = (\gamma_0/2 - 1)\rho^4 + (2 - \gamma_0/2)\rho^2.
\]  

(13)

Our simulations identified from the expression \(\gamma_0 = (\Delta W\Delta U)/(\langle\Delta U^2\rangle)\) (Ref. 3) the exponent \(\gamma_0 = 3.56\) at the state point \((\rho, T) = (1, 1)\). Equation (13) with \(\gamma_0 = 3.56\) was tested in two different ways. First, we compared at each state point along an isomorph the exponent \(\gamma(\rho)\) predicted from Eqs. (5) and (13) with that calculated from the fluctuations via \(\gamma = (\Delta W\Delta U)/(\langle\Delta U^2\rangle)\) (right panel of Fig. 2). The left panel presents a second test of Eq. (13) by showing results from simulating five temperatures at \(\rho = 1\), plotting for each temperature instantaneous values of the potential energy versus the potential energy of the same microconfigurations scaled to three other densities (\(\rho = 0.5, 1.6, 2.0\). The theory behind the observed straight lines is the following. Consider two isomorph 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: \(dU/dT = dU/T\). This implies \(dU/dU_0 = T/T_0\), i.e., \(\partial U/\partial U_0\) at \(\rho_0\) and \(\rho\) are equal. Integrating this at constant \(\rho_0\) and \(\rho\) leads to \(U = h(\rho_0)h(\rho) U_0 + \phi(\rho_0, \rho)\). 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”\(^{13}\) 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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