Isomorphs in Liquid State Diagrams

Results from Simulations

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Strong W-U Correlations in the Lennard-Jones liquid

Canonical Ensamble (NVT)

$$E = K(\mathbf{p}_1, \ldots, \mathbf{p}_N) + U(\mathbf{r}_1, \ldots, \mathbf{r}_N)$$

$$p = Nk_BT(\mathbf{p}_1, \ldots, \mathbf{p}_N)/V + W(\mathbf{r}_1, \ldots, \mathbf{r}_N)/V$$

The well studied Lennard-Jones liquid

$$U_{\text{pair}}(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

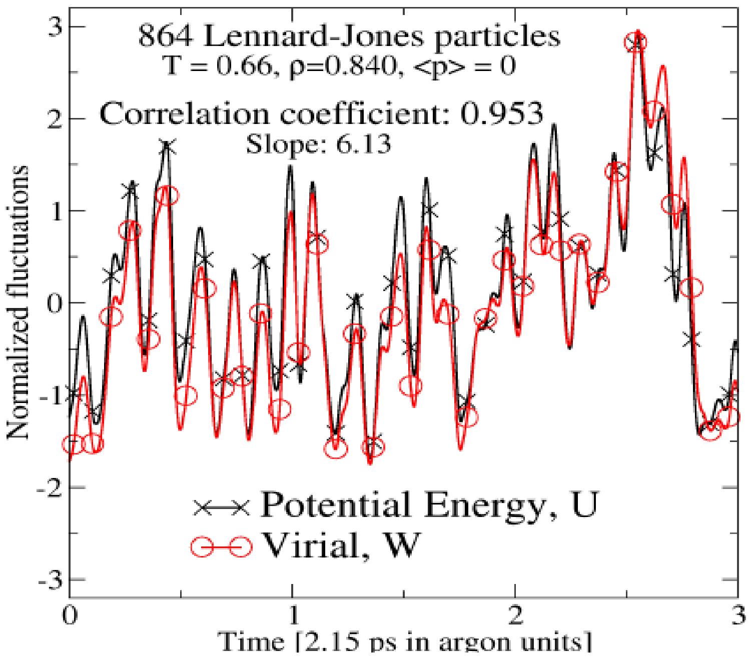
W(t) and U(t) are instantaneously correlated

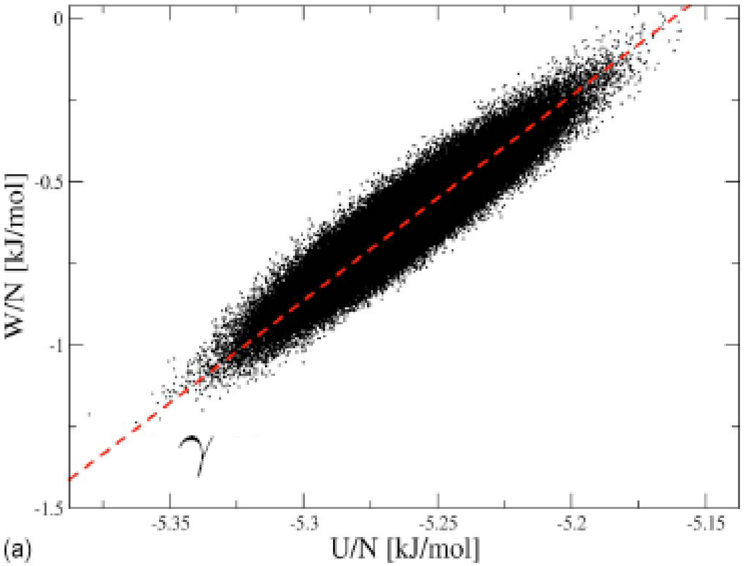
[Pedersen et al. PRL 100 015701 2008]

Two important numbers:

$$R \equiv \frac{\langle \Delta W \Delta U \rangle}{\sqrt{\langle (\Delta W)^2 \rangle \langle (\Delta U)^2 \rangle}} = 0.953 \;\&$$

$$\gamma \equiv \sqrt{\frac{\langle (\Delta W)^2 \rangle}{\langle (\Delta U)^2 \rangle}} = 6.13$$

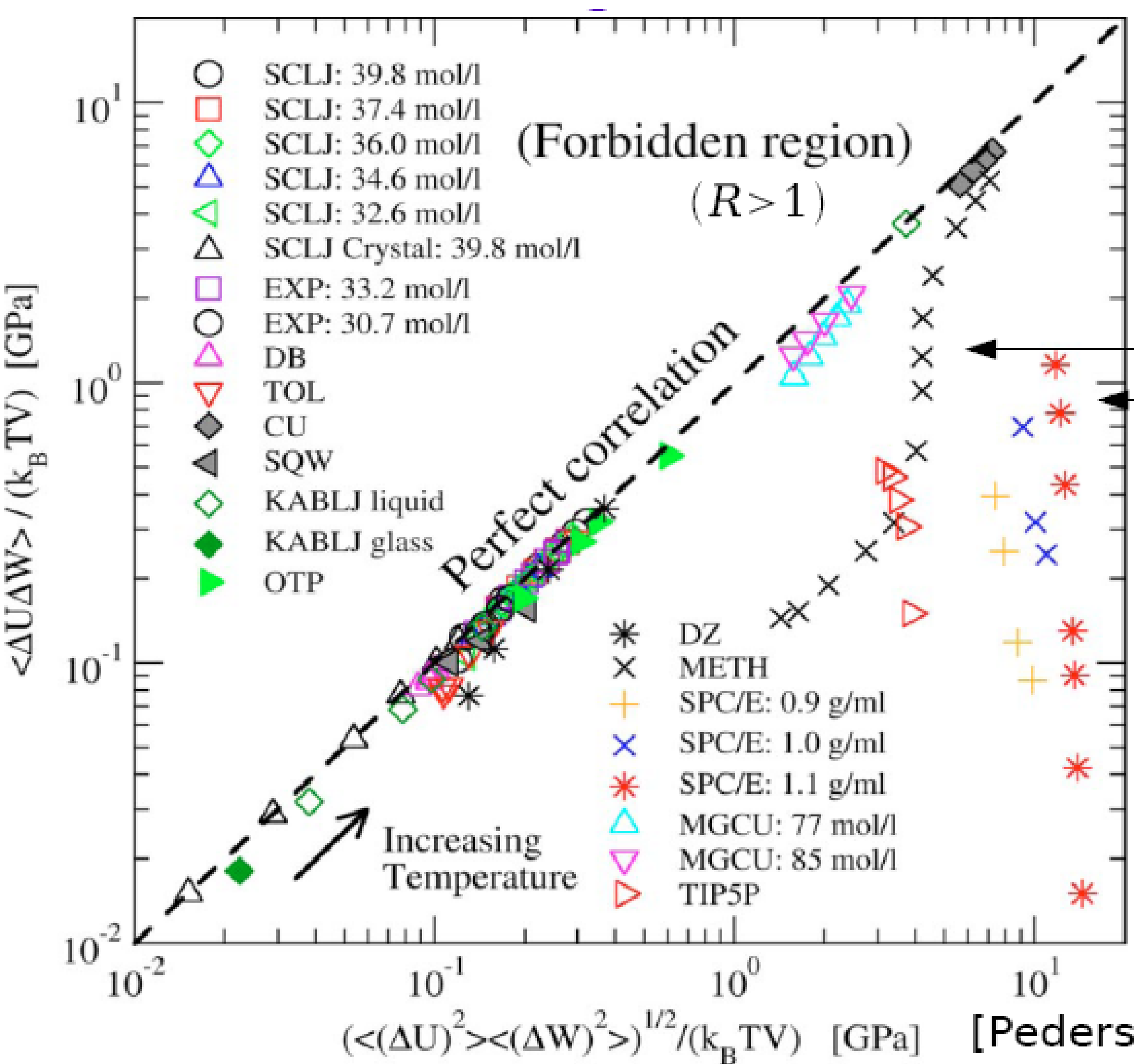




Questions

- Phenomenology: How general is this?
- Analysis: What causes such strong correlations?

Strongly Correlating Liquids (SCL)



Correlation coefficient:

$$R \equiv \frac{\langle \Delta W \Delta U \rangle}{\sqrt{\langle (\Delta W)^2 \rangle \langle (\Delta U)^2 \rangle}}$$

Competing interactions destroy the correlation:

$$U = U_{Coulomb} + U_{LJ}$$

$$W = W_{Coulomb} + W_{LJ}$$

Not correlated

Correlated

Correlated

[Pedersen et al. PRL (2008)]

[Bailey et al. JCP (2008), paper I]

Origin: Recall Soft-Sphere r^{-n} Liquids

Pair interaction of inverse power-law,

$$U_{\text{pair}} = \varepsilon \left(\frac{r}{\sigma}\right)^{-n}.$$

Pair virial,

$$W_{\text{pair}} = -\frac{1}{3} r \frac{\partial U_{\text{pair}}}{\partial r} = \frac{n\varepsilon}{3} \left(\frac{r}{\sigma}\right)^{-n}.$$

Thus ($U = \sum_{\text{pairs}} U_{\text{pair}}$ and $W = \sum_{\text{pairs}} W_{\text{pair}}$),

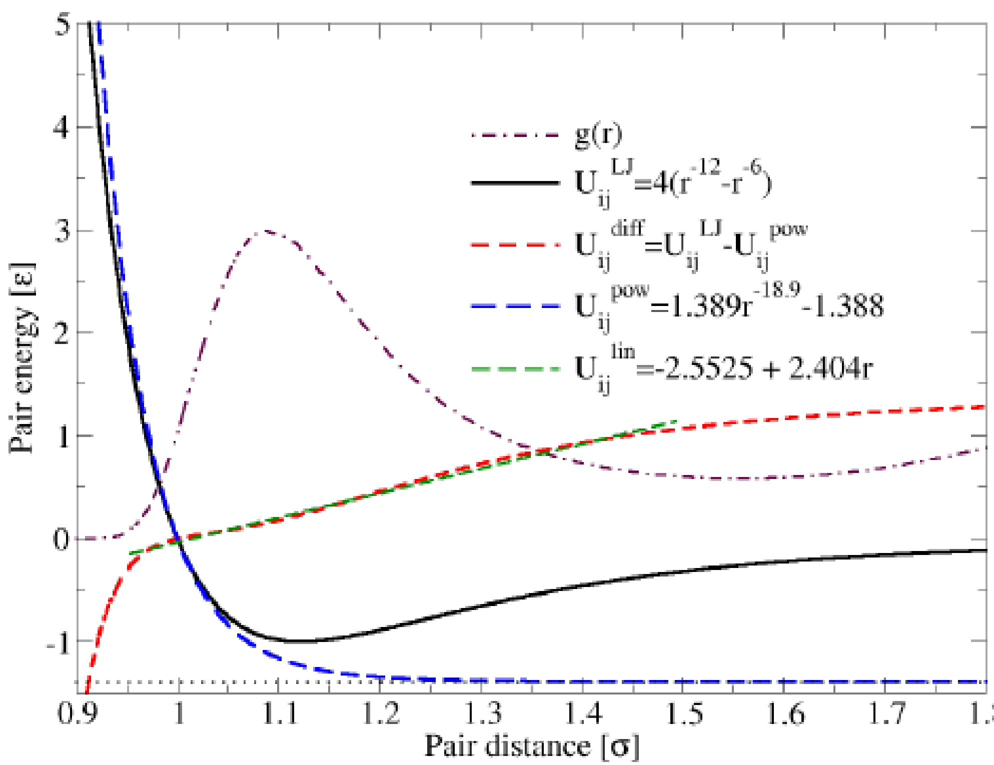
$$U = \gamma W$$

where

$$\gamma = n/3.$$

Correlation is exact $R = 1$ and trivial.

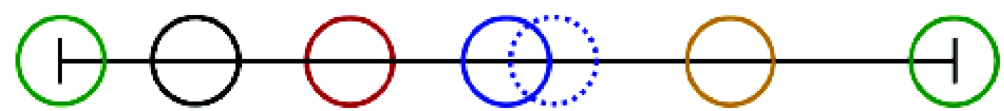
The Best IPL r^{-n} Describe Fluctuations



$U^{LJ} - U^{pow} \simeq br + c$, in the first peak of $g(r)$:

$$U^{LJ} = ar^{-n} + br + c + U^{rest}$$

One-dimensional system with only nearest neighbor interactions in a constant "volume" L:



$$\sum_{i>j} r_{ij} = L$$

$$\Downarrow$$

$$\sum_{i>j}(br_{ij} + c) = bL + Nc = [\text{constant}]$$

[Bailey et al., JCP 129:184508 (2008)]

Consequence:

Strongly correlating liquids inherit (some) scaling properties from the IPL potential.

Inverse Power Law Potentials (Thermodynamics)

Inverse power law potential (IPL)

$$v(r) = Ar^{-n}$$

$$F = F_{\rm id} + F_{\rm ex} \qquad F_{\rm id} = -Nk_BT\ln(\rho\Lambda^3)$$

The excess free energy is given by

$$e^{-F_{\rm ex}/k_BT} = \int \frac{d\mathbf{r}_1}{V}\cdots\frac{d\mathbf{r}_N}{V}e^{-U(\mathbf{r}_1,\ldots,\mathbf{r}_N)/k_BT}.$$

The excess free energy can be written as a function of density and temperature (Klein's theorem)

$$F_{\rm ex,IPL} = Nk_BT\phi\left(\rho^{n/3}/T\right)$$

This implies that a number of derived quantities are also a function of $\rho^{n/3}/T$.

Excess entropy

$$S_{\rm ex} = -(\partial F_{\rm ex}/\partial T)_V$$
$$S_{\rm ex,IPL} = Nk_B\, f_1\left(\rho^{n/3}/T\right)$$

Potential energy

$$U = F_{\rm ex} + TS_{\rm ex}$$
$$U_{\rm IPL} = Nk_BT\, f_2\left(\rho^{n/3}/T\right)$$

Virial

$$W = -V(\partial F_{\rm ex}/\partial V)_T$$
$$W_{\rm IPL} = \frac{n}{3}Nk_BT\, f_2\left(\rho^{n/3}/T\right)$$

Excess bulk modulus

$$K_T^{\rm ex} = V(\partial^2 F_{\rm ex}/\partial V^2)_T$$
$$K_{T,\rm IPL}^{\rm ex} = \rho k_BT\, f_3\left(\rho^{n/3}/T\right)$$

Excess specific heat

$$c_V^{\rm ex} = -(T/V)(\partial^2 F_{\rm ex}/\partial T^2)_V$$
$$c_{V,\rm IPL}^{\rm ex} = \rho k_B f_4\left(\rho^{n/3}/T\right)$$

$$f_1(x) = x\phi'(x) - \phi(x),\ f_2(x) = x\phi'(x),\ f_3(x) = (n/3)^2x^2\phi''(x) + [(n/3) + (n/3)^2]x\phi'(x)$$

$$f_4(x) = -x^2\phi''(x)$$

Inverse Power Law Potentials (Dynamics)

Consider the standard molecular dynamics (MD) case where the equations of motion are Newton's equations

$\mathbf{r}_i(t)\ (i = 1, ..., N)$ Solution to Newton's equations ← State point (T_0, ρ_0)

then

$\mathbf{r}_i^{(1)}(t) = \alpha \mathbf{r}_i(\lambda t)$ is a solution if $\alpha^{-(n+2)} = \lambda^2$ ← State point $(T_1 = T_0\, \alpha^2 \lambda^2,\ \rho_1 = \rho_0 / \alpha^3)$

This implies:

$$T_1 = \alpha^{-n} T_0 = \left(\frac{\rho}{\rho_0}\right)^{n/3} T_0$$

two states with different densities and temperatures but same $\rho^{n/3}/T$ *have dynamics that scale into one*

$$\tilde{\tau} = f_5\left(\rho^{n/3}/T\right),$$

$$\tilde{D} = f_6\left(\rho^{n/3}/T\right).$$

Inheritance of Scaling Properties by Generalized IPL Potentials

The existence of isomorphs is a consequence of the hidden scale invariance characterizing strongly correlating liquids.

$$v_{ij}(r_{ij}) = \epsilon_{ij}\left(\frac{\sigma_{ij}}{r_{ij}}\right)^n + v_{ij}^{\mathrm{diff}}(r_{ij}) \qquad U_{\mathrm{diff}}(\mathbf{r}_1, ..., \mathbf{r}_N) = f(V)$$

Excess free energy

$$e^{-F_{\mathrm{ex}}/k_BT} = e^{-f(V)/k_BT}\int \frac{d\mathbf{r}_1}{V}\cdots\frac{d\mathbf{r}_N}{V}e^{-U_{\mathrm{IPL}}(\mathbf{r}_1,\ldots,\mathbf{r}_N)/k_BT}$$

$$F_{\mathrm{ex}} = f(V) + F_{\mathrm{ex,IPL}} = f(V) + Nk_BT\phi\left(\rho^{n/3}/T\right) \quad ✗$$

$$S_{\mathrm{ex}} = S_{\mathrm{ex,IPL}} = Nk_B\, f_1\left(\rho^{n/3}/T\right), \quad ✓$$

$$U = f(V) + U_{\mathrm{IPL}} = f(V) + Nk_BT\, f_2\left(\rho^{n/3}/T\right), \quad ✗$$

$$W = -f'(V)V + W_{\mathrm{IPL}} = -f'(V)V + \frac{n}{3}Nk_BT\, f_2\left(\rho^{n/3}/T\right), \quad ✗$$

$$K_T^{\mathrm{ex}} = V f''(V) + K_{T,\mathrm{IPL}}^{\mathrm{ex}} = V f''(V) + \rho k_BT\, f_3\left(\rho^{n/3}/T\right), \quad ✗$$

$$c_V^{\mathrm{ex}} = c_{V,\mathrm{IPL}}^{\mathrm{ex}} = \rho k_B f_4\left(\rho^{n/3}/T\right), \quad ✓$$

$$\beta_V^{\mathrm{ex}} = \beta_{V,\mathrm{IPL}}^{\mathrm{ex}} = \frac{n}{3}\rho k_B\, f_4\left(\rho^{n/3}/T\right). \quad ✓$$

Quantities having contributions from the f(V)-term do not obey IPL scaling

Scaling behavior for dynamics and structure is inhereted ✓

Definition of Isomorphs

[Gnan et al., JCP 131: 234504 (2009)]

Two state points (1) and (2) with temperatures T_1 and T_2 and densities ρ_1 and ρ_2 are *isomorphic* if :

Given two configurations

$$(\mathbf{r}_1^{(1)}, \ldots, \mathbf{r}_N^{(1)}) \text{ and } (\mathbf{r}_1^{(2)}, \ldots, \mathbf{r}_N^{(2)})$$

which are related by

$$\tilde{\mathbf{r}}_i^{(1)} = \tilde{\mathbf{r}}_i^{(2)} \quad \text{where} \quad \tilde{\mathbf{r}}_i \equiv \rho^{1/3}\mathbf{r}_i$$

they have proportional configurational NVT Boltzmann factors:

$$e^{-U(\mathbf{r}_1^{(1)}, \ldots, \mathbf{r}_N^{(1)})/k_B T_1} = C_{12}\, e^{-U(\mathbf{r}_1^{(2)}, \ldots, \mathbf{r}_N^{(2)})/k_B T_2}$$

Properties (isomorph invariants):

- Equal Boltzmann probability:

$$P(\mathbf{r}_1, \ldots, \mathbf{r}_N) = e^{-[U(\mathbf{r}_1, \ldots, \mathbf{r}_N) - F_{\rm ex}]/k_B T} .$$

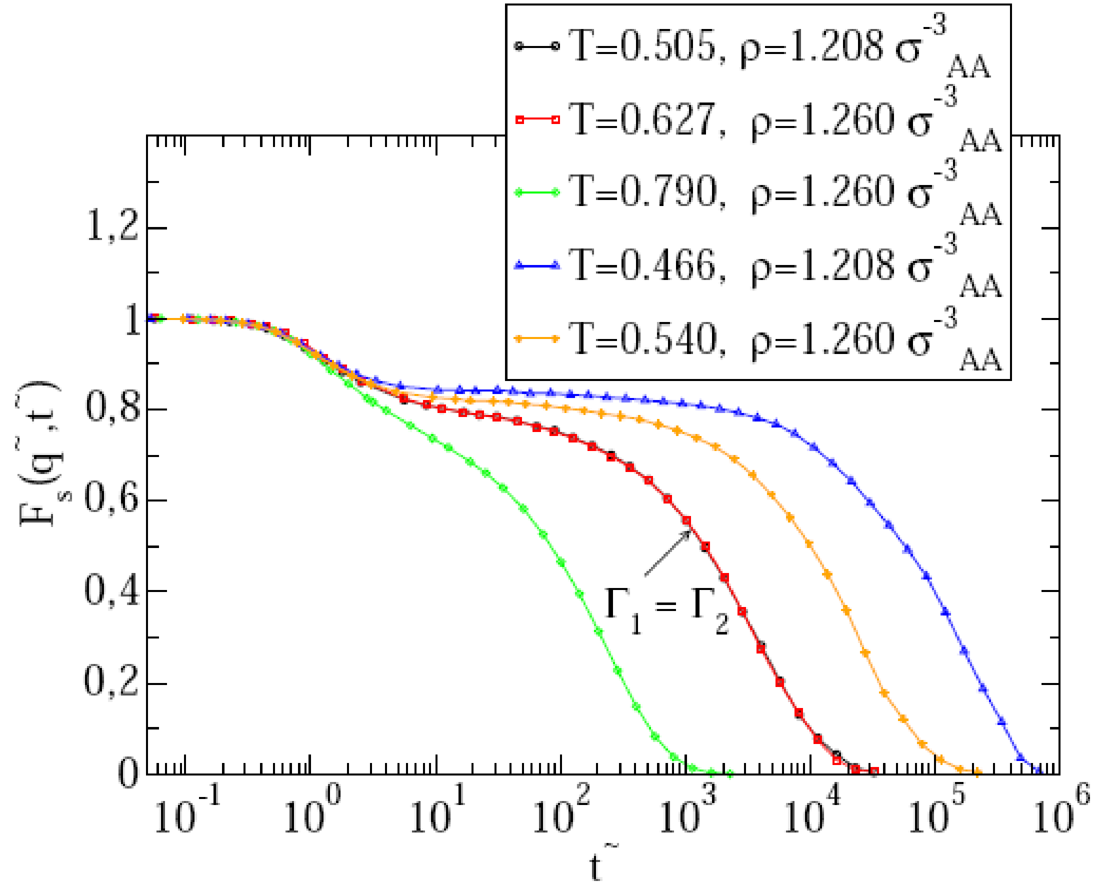
- Equal entropy: $S_{\rm ex} = -\partial F_{\rm ex}/\partial T$

- Both NVE and NVT Newtonian dynamics as well as Brownian dynamics are isomorph invariant when described in reduced units

- Reduced transport coeffcients like the diffusion constant, the viscosity, etc., are invariant along an isomorph.

Simulation Results (Equilibrium Dynamics):

Normalized time-autocorrelation functions - as well as normalized higher-order time correlation functions - are invariant along an isomorph when quoted in reduced units



(8000 particles of KABLJ (80:20))

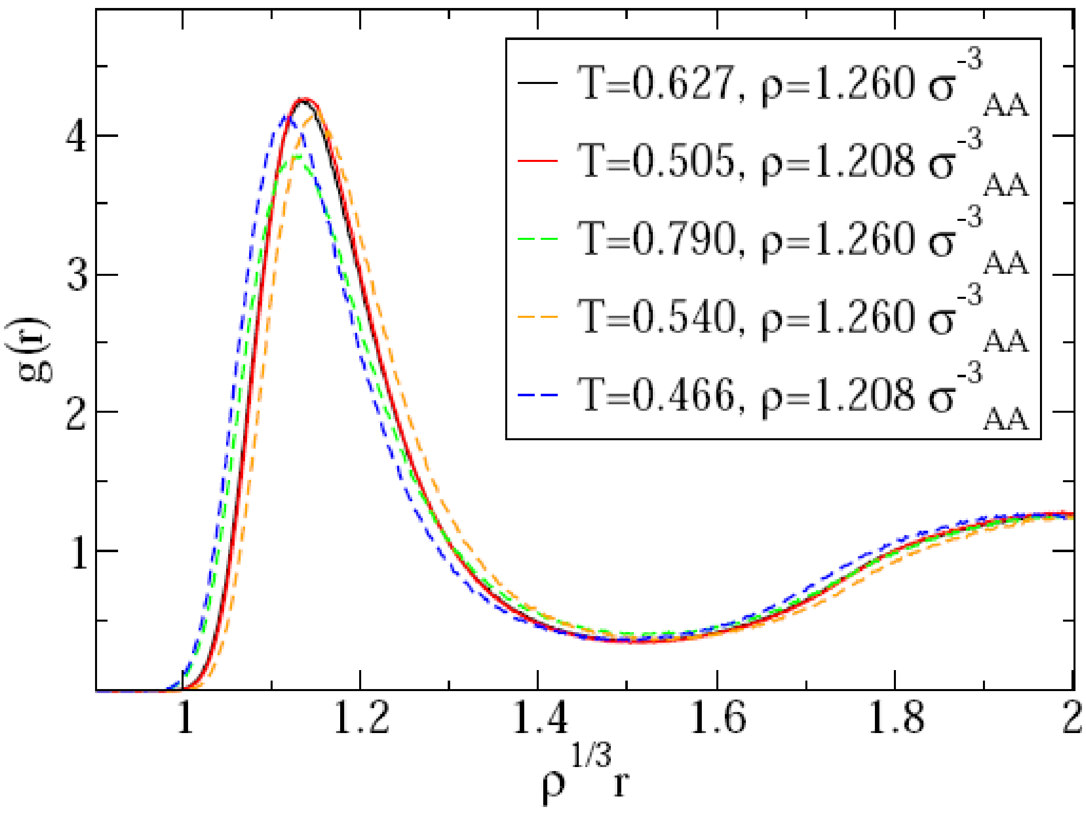
Isomorphic points are isochronic points, i.e the density scaling relation

$$\tau_\alpha = F(\rho^\gamma / T) = F(\Gamma)$$

holds.

Simulation Results (Structure):

Scaled radial distribution function(s) - as well as higher-order equilibrium particle probability distributions - are invariant along an isomorph.



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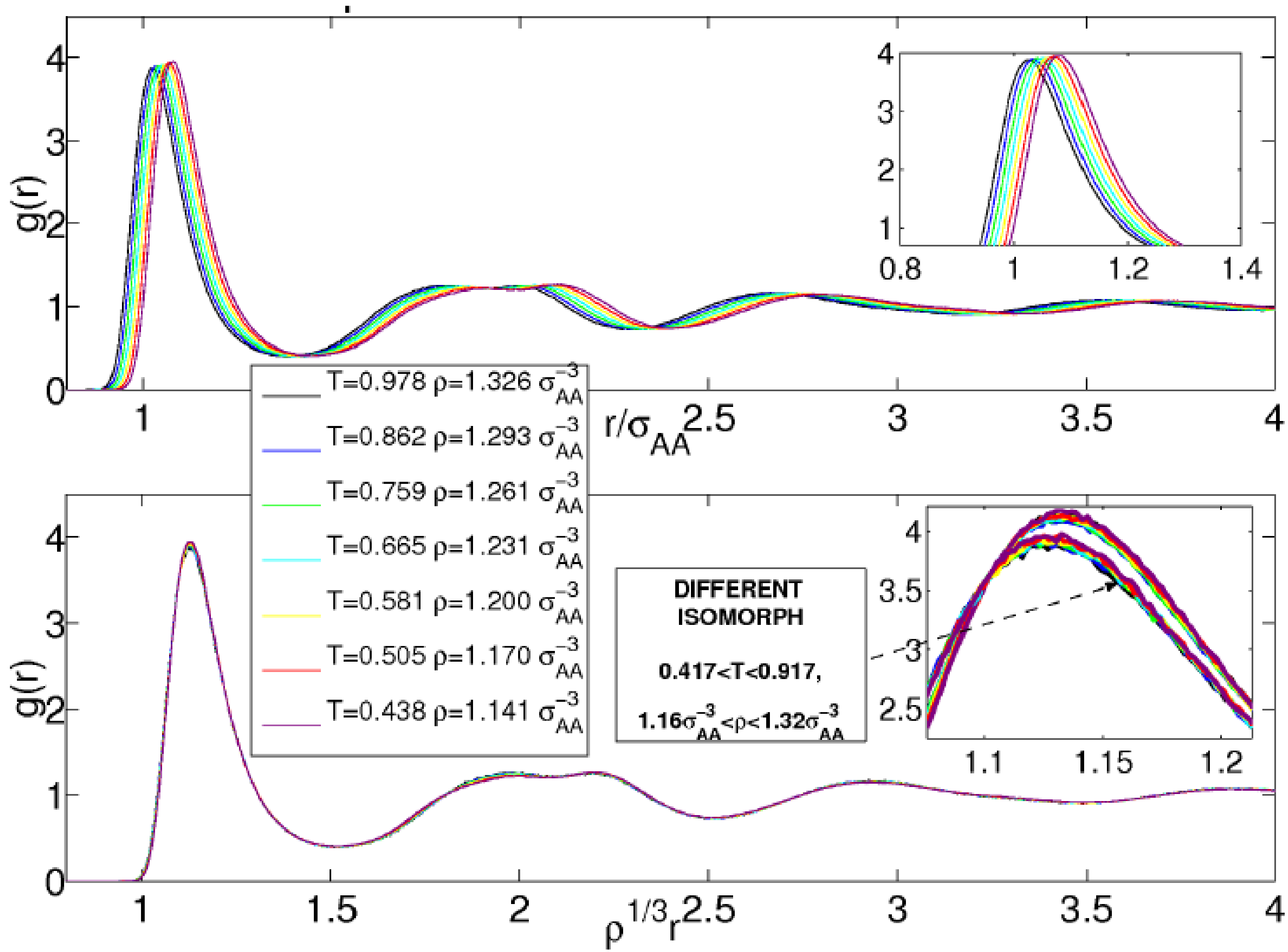

Simulation Results (Aging):

A jump between two isomorphic state points starting from equilibrium takes the system instantaneously to equilibrium.
(non-isomorphic transformations bring the system out of equilibrium)

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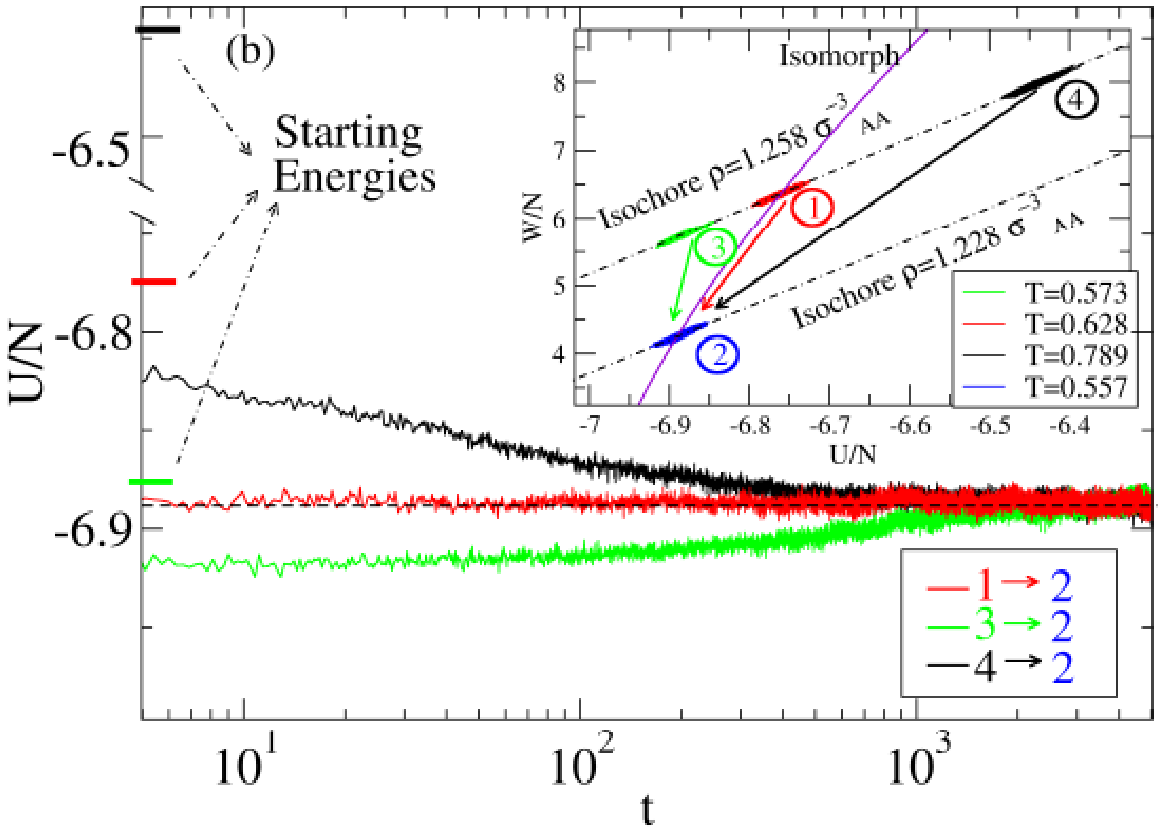

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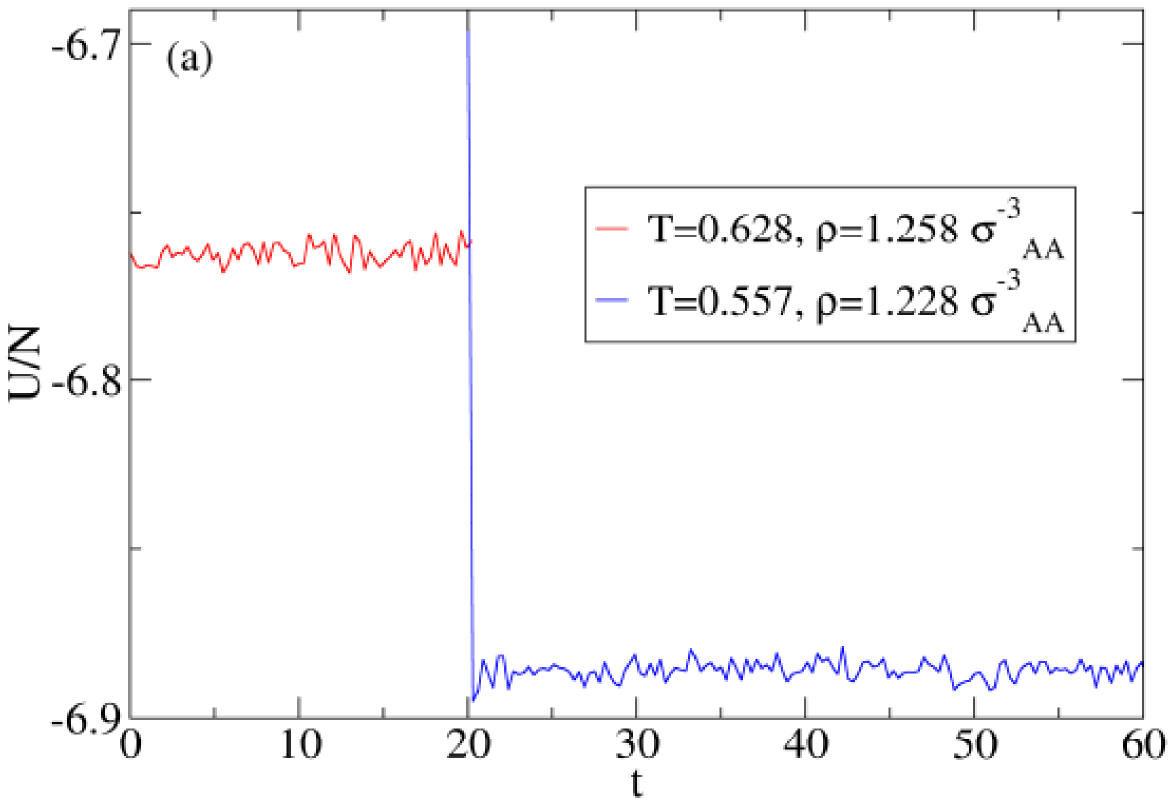
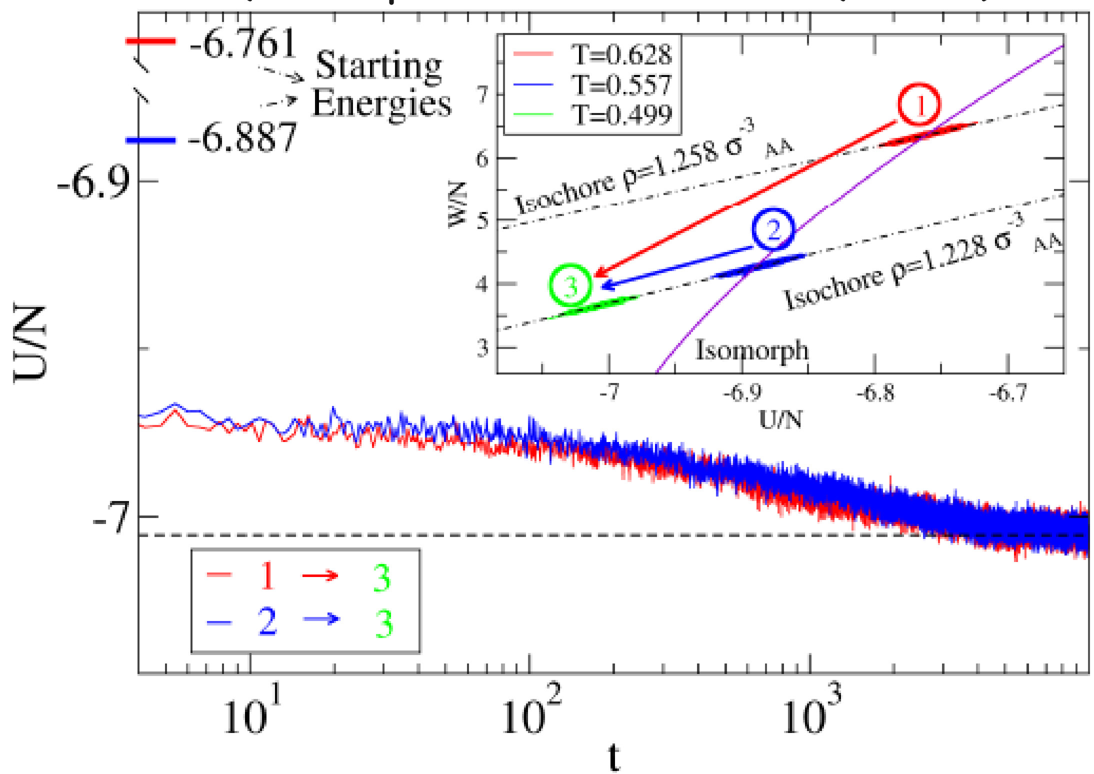


Simulation Results (Aging):

Jumps from any two isomorphic equilibrium state points to a third state point lead to the same aging behavior for all physical quantities.

(8000 particles of KABLJ (80:20)



Comparing Simulation Results with Theory:

Theory for generalized 12-6 Lennard-Jones potentials:

$$\phi_{ij}(r_{ij}) = \phi_{ij}^{(n)}(r_{ij}) + \phi_{ij}^{(m)}(r_{ij})$$

Equations of isomorphs in the (U-W) plane

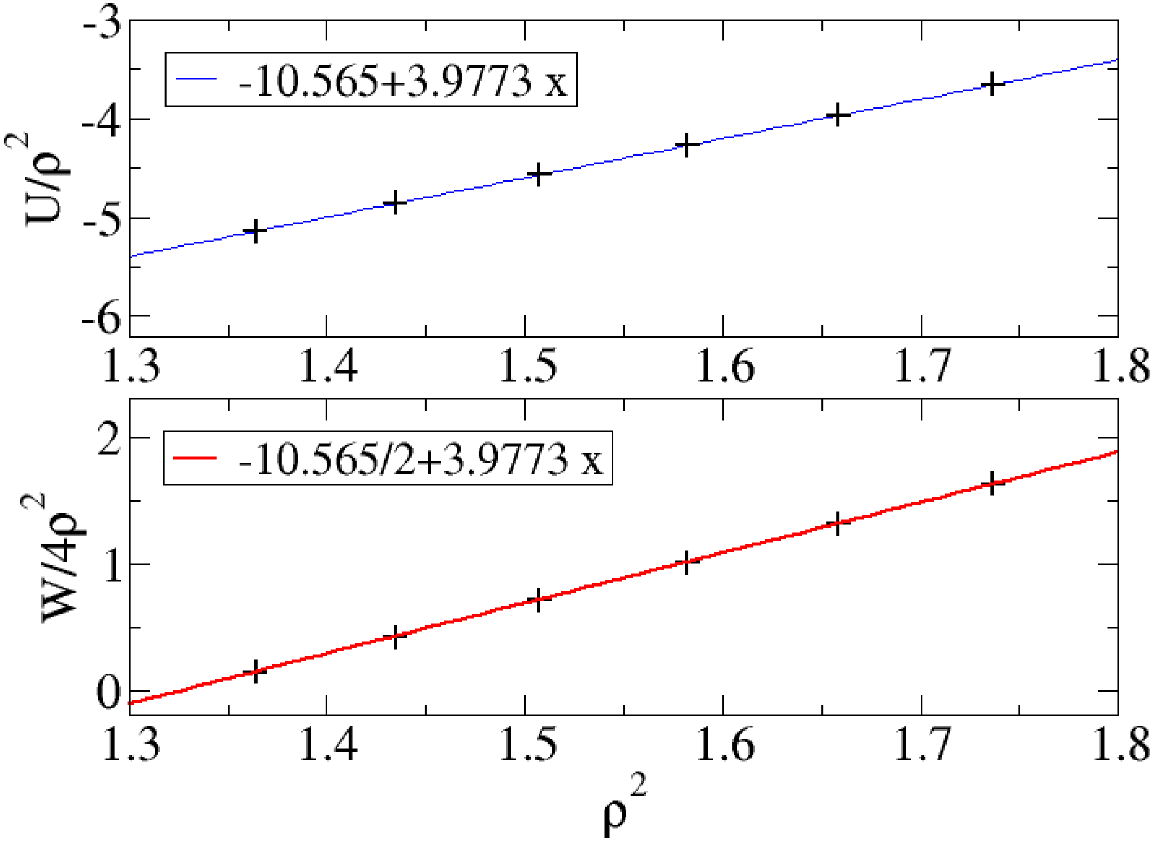
$$U = U_{12}^{*}\tilde{\rho}^{4} + U_{6}^{*}\tilde{\rho}^{2}$$

$$W = 4U_{12}^{*}\tilde{\rho}^{4} + 2U_{6}^{*}\tilde{\rho}^{2}$$

$$U_m \equiv \sum_{i<j}\phi_{ij}^{(m)}(r_{ij})$$

$$\phi_{ij}^{(m)}(r_{ij}) = \varepsilon_{ij}^{(m)}(\sigma_{ij}^{(m)}/r_{ij})^{m}$$

$$\tilde{\rho} \equiv (\rho/\rho^{*})$$



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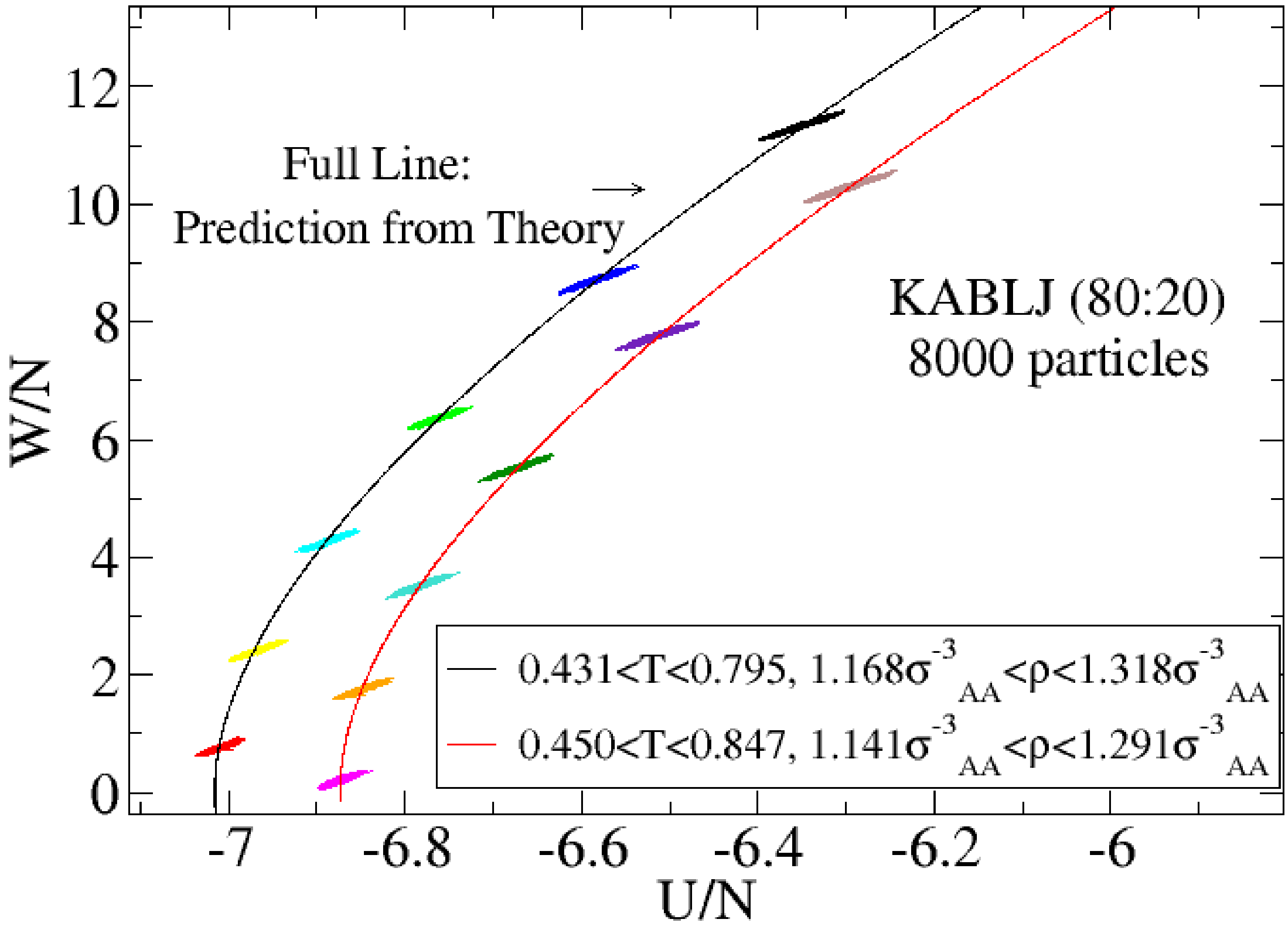


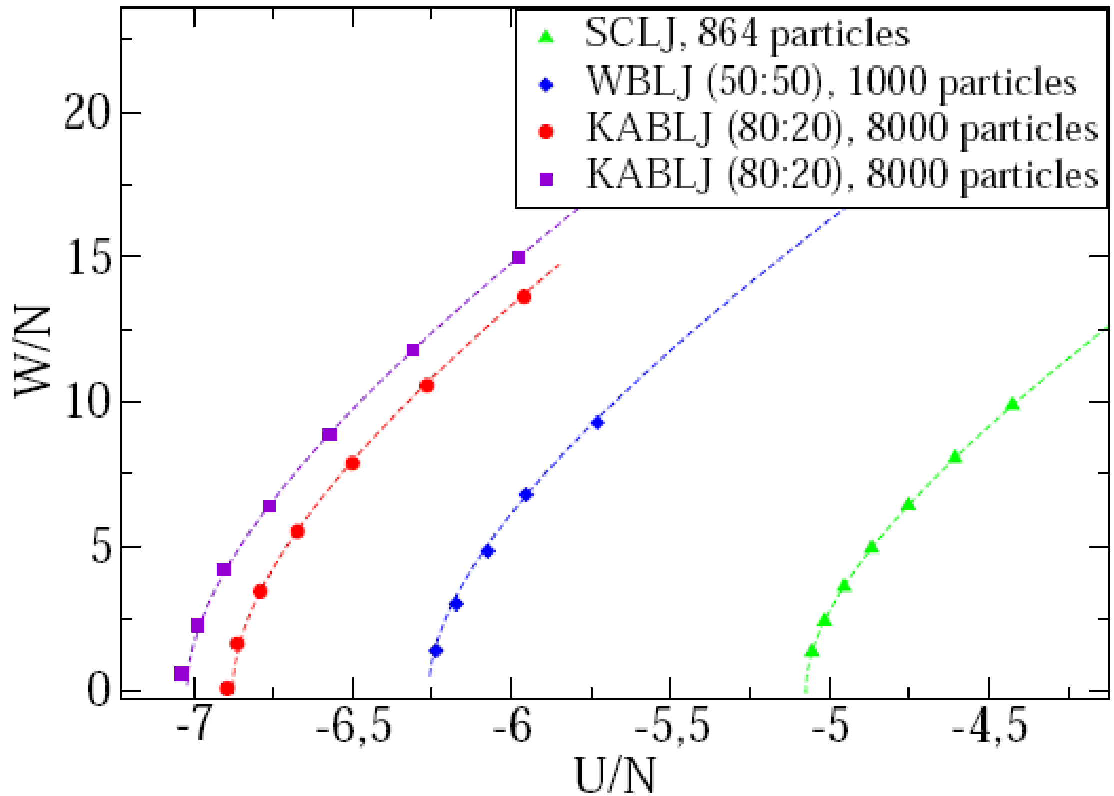
The Master Isomorph

From the two equations of isomorphs we can chose as reference point ($W^* = W^*_0$, $U^* = 0$)

$$W_0^* = \frac{(W-4U)^2}{W-2U}$$

Solving for W/W^*_0 we find:

$$\frac{W}{W_0^*} = \frac{(8U/W_0^*+1) \pm \sqrt{(8U/W_0^*+1)}}{2}, \quad \frac{U}{W_0^*} \geq -\frac{1}{8}$$



isomorphs are rotated parabolas in the U-W plane and are identical in scaled units

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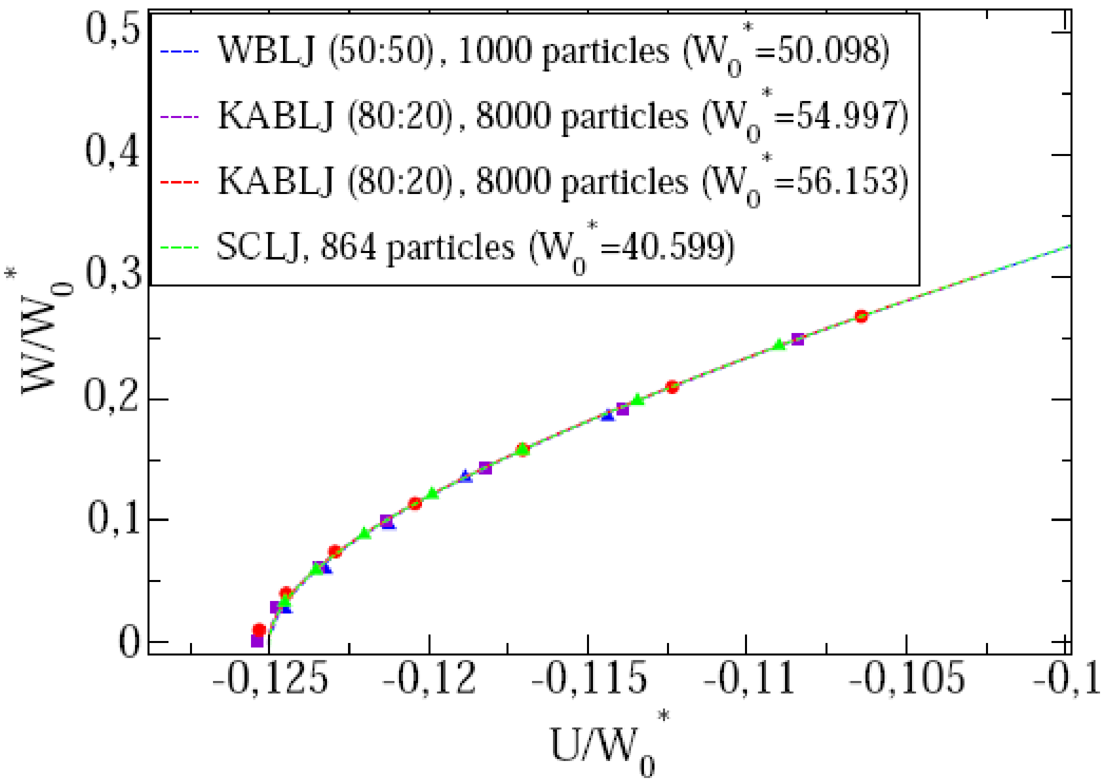

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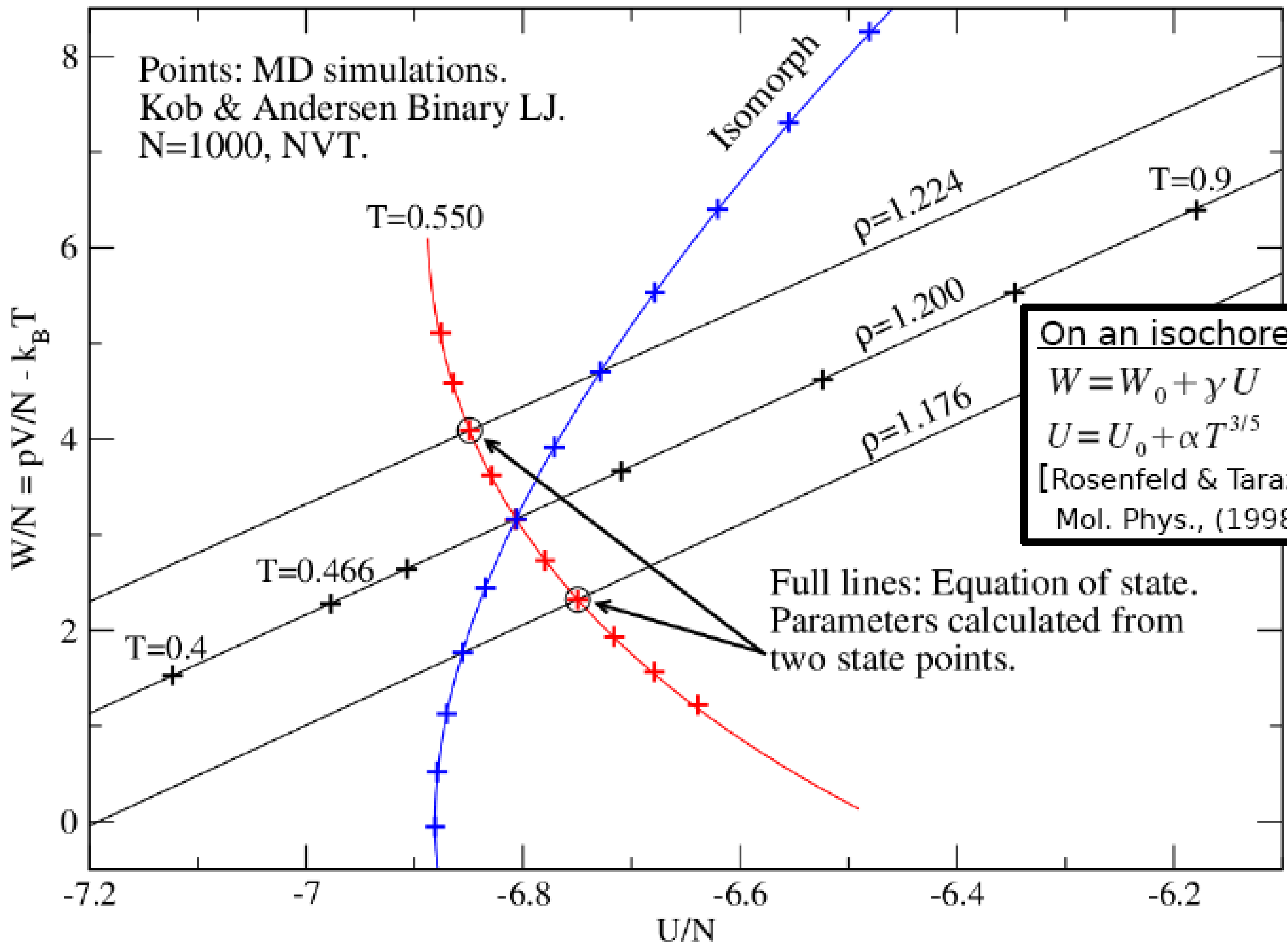
Understanding Isomorphs and Isochores Leads to an Equation of State



On an isochore:

$W = W_0 + \gamma U$

$U = U_0 + \alpha T^{3/5}$

[Rosenfeld & Tarazona, Mol. Phys., (1998)]

“Isomorphic” equation of state for KA BLJ

$$T_*(\rho,T) = T\tilde{\rho}^{-\gamma}, \quad \tilde{\rho} \equiv \rho/\rho_* \tag{11}$$

$$U_*(\rho,T) = \underline{U_0} + \underline{\alpha}(T\tilde{\rho}^{-\gamma})^{3/5} \tag{12}$$

$$W_*(\rho,T) = \underline{W_0} + \underline{\gamma}U_*(\rho,T) \tag{13}$$

From (U_*, W_*) we can calculate the contribution to the potential energy from the two IPL terms of the potential:

$$U_{m,*}(\rho,T) = \frac{-3W_*(\rho,T) + nU_*(\rho,T)}{n-m} = \frac{-3W_0 + (n-3\gamma)U_*(\rho,T)}{n-m} \tag{14}$$

$$U_{n,*}(\rho,T) = \frac{3W_*(\rho,T) - mU_*(\rho,T)}{n-m} = \frac{3W_0 - (m-3\gamma)U_*(\rho,T)}{n-m} \tag{15}$$

Finally we use isomorphic scaling to go back to the (ρ, T, U, W) state point:

$$U(\rho,T) = \tilde{\rho}^{n/3}U_{n,*}(\rho,T) + \tilde{\rho}^{m/3}U_{m,*}(\rho,T) \tag{16}$$

$$W(\rho,T) = \frac{n}{3}\tilde{\rho}^{n/3}U_{n,*}(\rho,T) + \frac{m}{3}\tilde{\rho}^{m/3}U_{m,*}(\rho,T) \tag{17}$$

Conclusions:

- We showed the existence of “approximated” isomorphs in the U-W plane for Lennard-Jones Liquids using molecular dynamics simulations.

- Starting from one reference point in the U-W plane we are able to identify a set of isomorphic points (isomorphic curve) and predict a numbet of thermodynamic dynamic and structural equilibrium properties as well as off-equilibrium properties (we can predict effective temperatures of glasses!!).

- Isomorphs’ shape depends only on the exponent of the interacting potentials and not from their parameters, thus isomorphs with the same “kind” of potential collapse into a master isomorph.

- Isomorphic state points are a feature of only strongly correlating liquids.