Systems with hidden scale invariance: An overview of the isomorph theory. II

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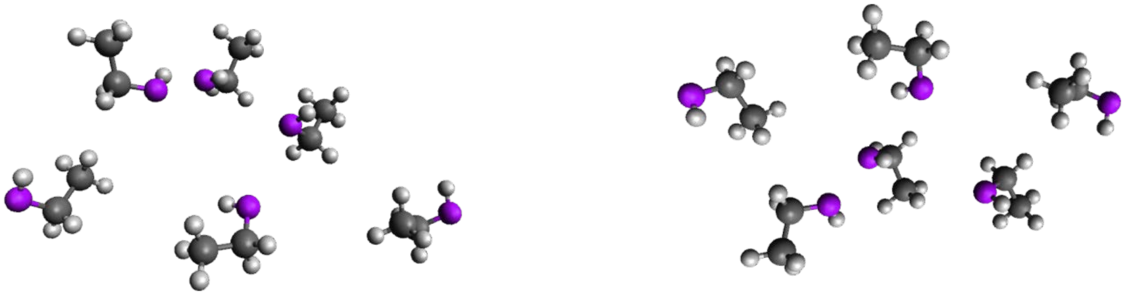
Glass
&time

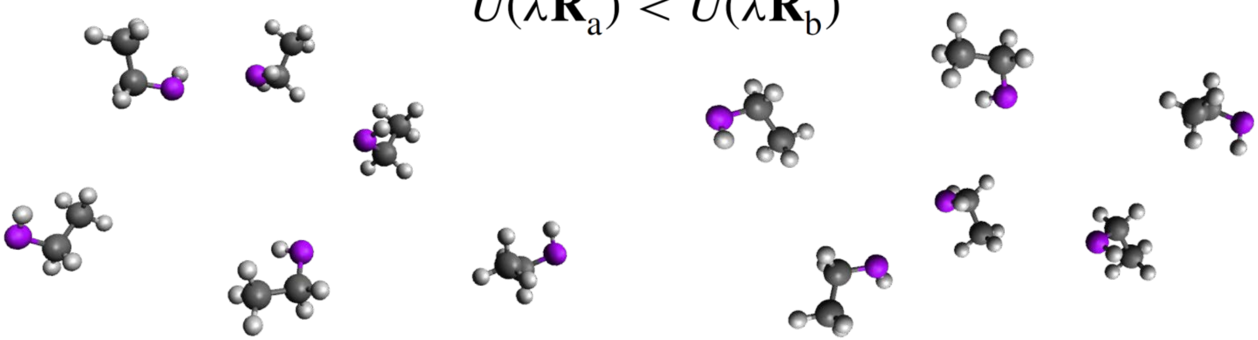
”Hidden” scale invariance: Isomorph theory v2 (2014)



$$U(\mathbf{R}_{\rm a}) < U(\mathbf{R}_{\rm b})$$

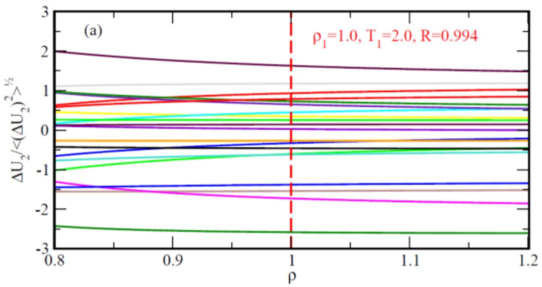
$$\Downarrow$$

$$U(\lambda\mathbf{R}_{\rm a}) < U(\lambda\mathbf{R}_{\rm b})$$

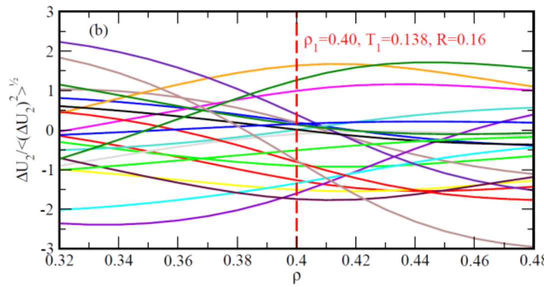


Isomorph theory, v2

[J. Chem. Phys. **141**, 204502 (2014)]



Lennard-Jones



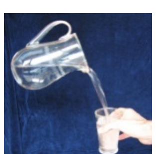
Lennard-Jones Gaussian

$$U(\mathbf{R}_\mathrm{a}) < U(\mathbf{R}_\mathrm{b}) \;\Rightarrow\; U(\lambda\mathbf{R}_\mathrm{a}) < U(\lambda\mathbf{R}_\mathrm{b})$$ ("R-simple")

$$U(\mathbf{R}_\mathrm{a}) = U(\mathbf{R}_\mathrm{b}) \;\Rightarrow\; U(\lambda\mathbf{R}_\mathrm{a}) = U(\lambda\mathbf{R}_\mathrm{b})$$

$$\mathbf{R}_a \cdot \nabla U(\lambda\mathbf{R}_a) = \mathbf{R}_b \cdot \nabla U(\lambda\mathbf{R}_b)$$

$$W(\mathbf{R}) \equiv -\frac{1}{3}\mathbf{R}\cdot\nabla U(\mathbf{R})$$



i.e., *strong virial-potential energy correlations*

Isomorph theory, contd.

Length unit: $\rho^{-1/3}$ Energy unit: $k_B T$ Time unit: $\rho^{-1/3}\sqrt{m/k_B T}$

Define the microscopic entropy: $S_{\rm ex}(\mathbf{R}) \equiv S_{\rm ex}(\rho, U(\mathbf{R}))$

Two configurations with same reduced coordinates: $\rho_1^{1/3}\mathbf{R}_1 = \rho_2^{1/3}\mathbf{R}_2$

$$S_{\rm ex}(\mathbf{R}_1)/k_B \;=\; -N\ln N \;+\; \ln\left(\mathrm{Vol}\{\tilde{\mathbf{R}}'\,|\,U(\rho_1^{-1/3}\tilde{\mathbf{R}}') < U(\mathbf{R}_1)\}\right)$$

$$S_{\rm ex}(\mathbf{R}_2)/k_B \;=\; -N\ln N \;+\; \ln\left(\mathrm{Vol}\{\tilde{\mathbf{R}}'\,|\,U(\rho_2^{-1/3}\tilde{\mathbf{R}}') < U(\mathbf{R}_2)\}\right)$$

Applying $\lambda = \rho_2^{-1/3}\rho_1^{1/3}$ leads to identity, i.e. ($\tilde{\mathbf{R}} \equiv \rho^{1/3}\mathbf{R}$)

$$U(\mathbf{R}) = U(\rho, S_{\rm ex}(\tilde{\mathbf{R}}))$$

Isomorph theory, contd. $U(\mathbf{R}) = U(\rho, S_{\rm ex}(\tilde{\mathbf{R}}))$

1) *Invariant structure and dynamics along the configurational adiabats*

$$\tilde{\mathbf{F}} \equiv \mathbf{F}\rho^{-1/3}/k_B T \qquad\qquad d^2\tilde{\mathbf{R}}/d\tilde{t}^2 = \tilde{\mathbf{F}}$$

$$\nabla = \rho^{1/3}\tilde{\nabla} \qquad\qquad \mathbf{F} = -\nabla U = -(\partial U/\partial S_{\rm ex})_\rho\, \rho^{1/3}\tilde{\nabla} S_{\rm ex}(\tilde{\mathbf{R}})$$

$$\tilde{\mathbf{F}} = -\tilde{\nabla} S_{\rm ex}(\tilde{\mathbf{R}})/k_B$$

2) *Invariant Boltzmann probabilities along the configurational adiabats*

$$U(\mathbf{R}) \cong U + T(\rho, S_{\rm ex})\left(S_{\rm ex}(\tilde{\mathbf{R}}) - S_{\rm ex}\right)$$

Two configurations on config. adiabat with same reduced coordinates obey

$$\frac{U(\mathbf{R}_1) - U_1}{k_B T_1} \cong \frac{U(\mathbf{R}_2) - U_2}{k_B T_2}$$

$$\exp(-U(\mathbf{R}_1)/k_B T_1) \cong C_{12} \exp(-U(\mathbf{R}_2)/k_B T_2)$$

”Hidden scale invariance”

R-simple systems obey

$$U(\mathbf{R}) = U(\rho, S_{\text{ex}}(\tilde{\mathbf{R}}))$$

<u>This class includes most:</u>

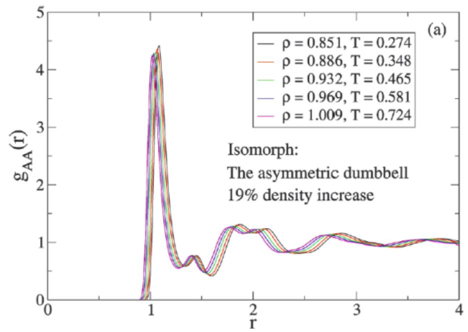
- metals
- van der Waals bonded systems
- weakly ionic/dipolar systems

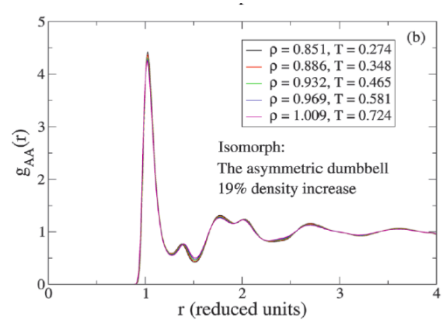
<u>This class excludes most:</u>

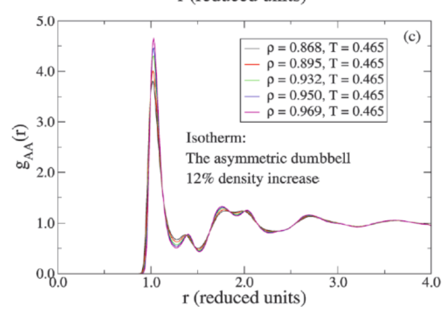
- covalently and hydrogen-bonded systems,
- strongly ionic or dipolar systems

Asymmetric dumbbell model

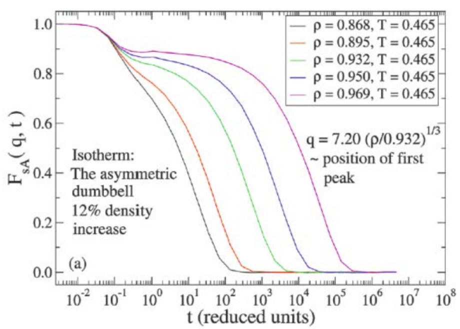
[J. Phys. Chem. B **116**, 1008 (2012)]

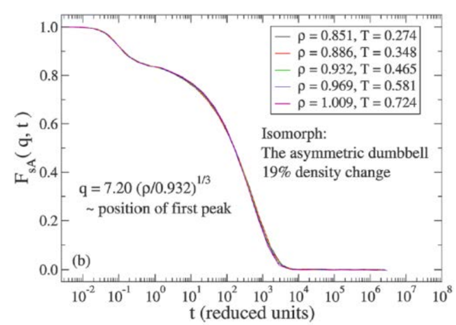




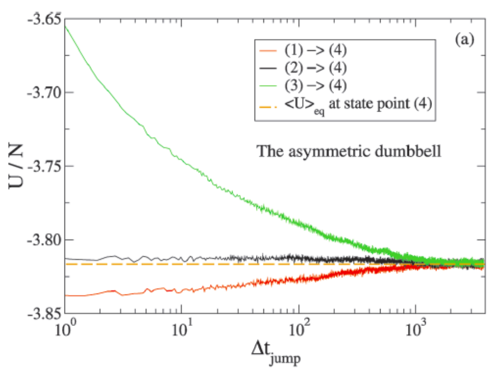


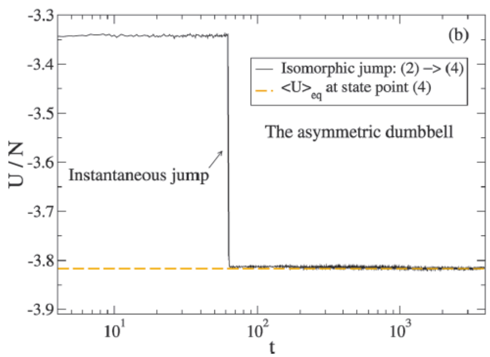
Dynamics:





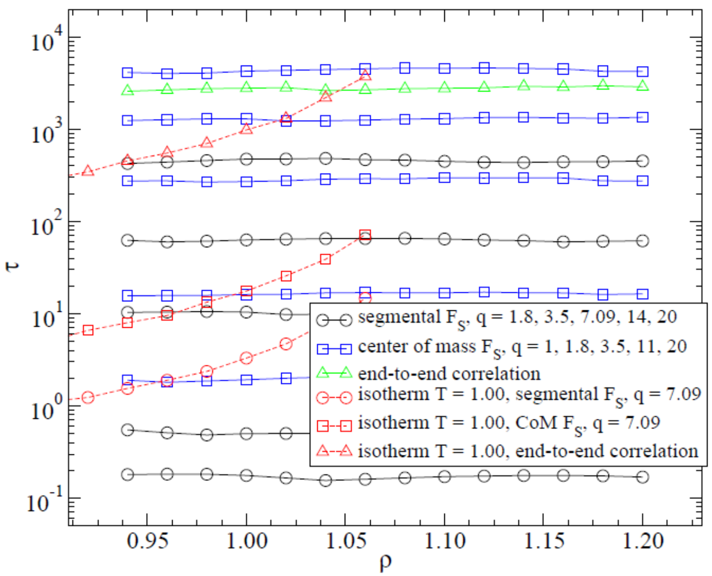
Isomorph jump:

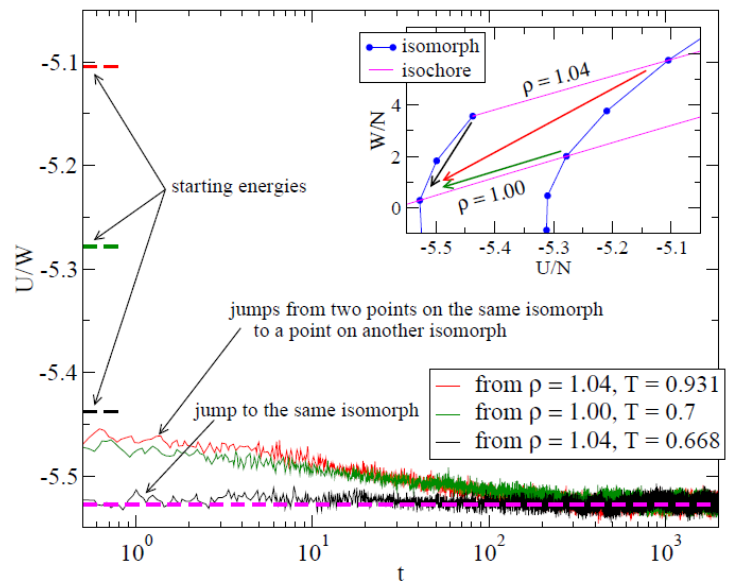


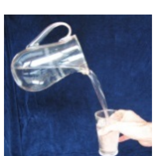


The 10-bead flexible Lennard-Jones chain

[J. Chem. Phys. **141**, 054904 (2014)]

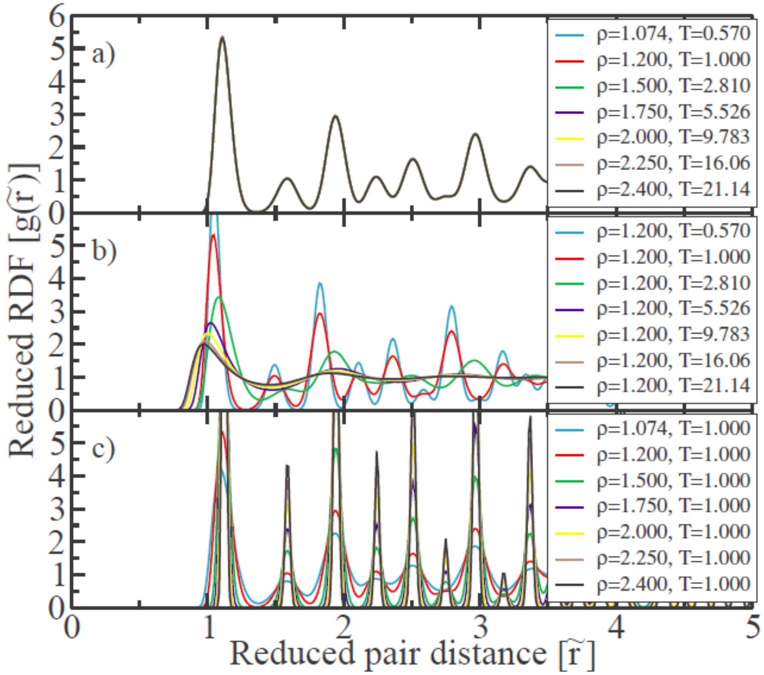


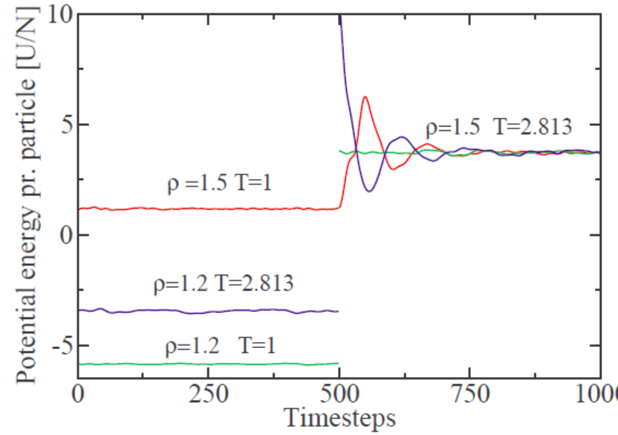




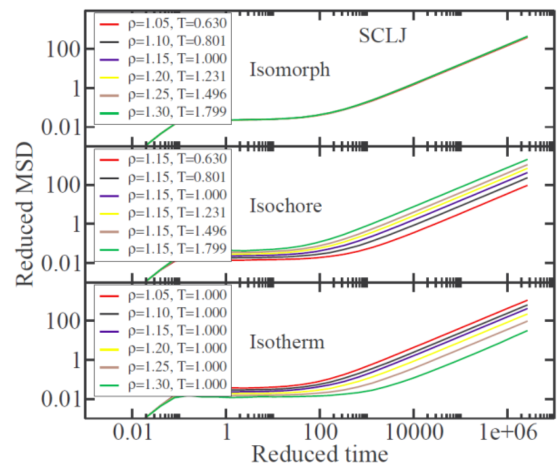
LJ face-centered cubic crystal

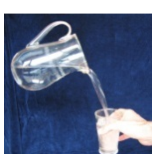
[Phys. Rev. B **90**, 094106 (2014)]





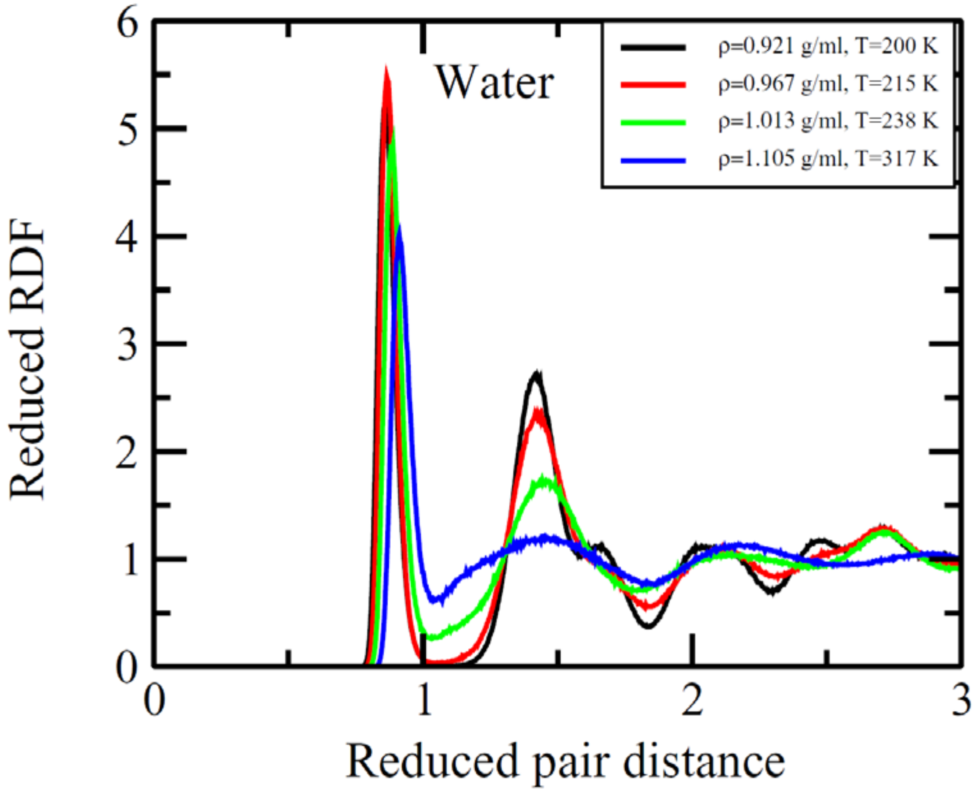
With defects:





SPC/E hexagonal ice

[Phys. Rev. B **90**, 094106 (2014)]



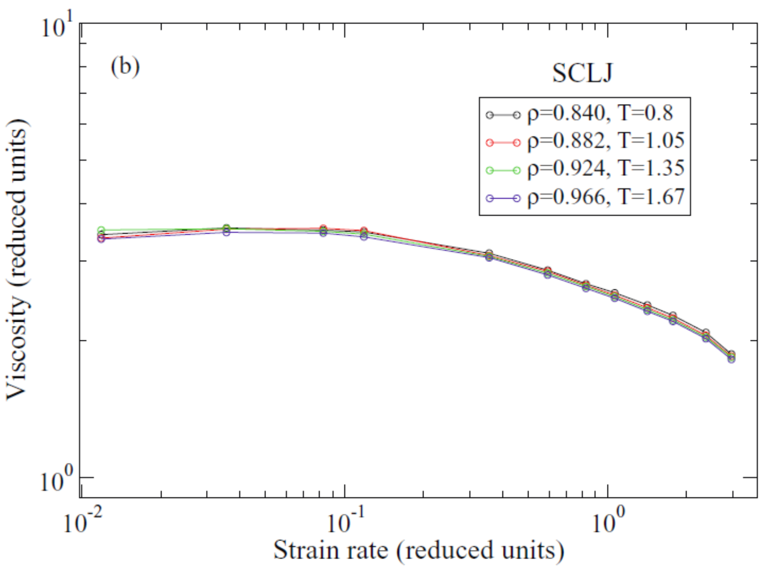
Isomorph invariance of the SLLOD equations of motion for shearing liquids

[J. Chem. Phys. **138**, 1554505 (2013), with Leila Separdar]

$$\dot{\mathbf{r}}_i = \mathbf{p}_i/m_i + \mathbf{r}_i \cdot \nabla \mathbf{v},$$

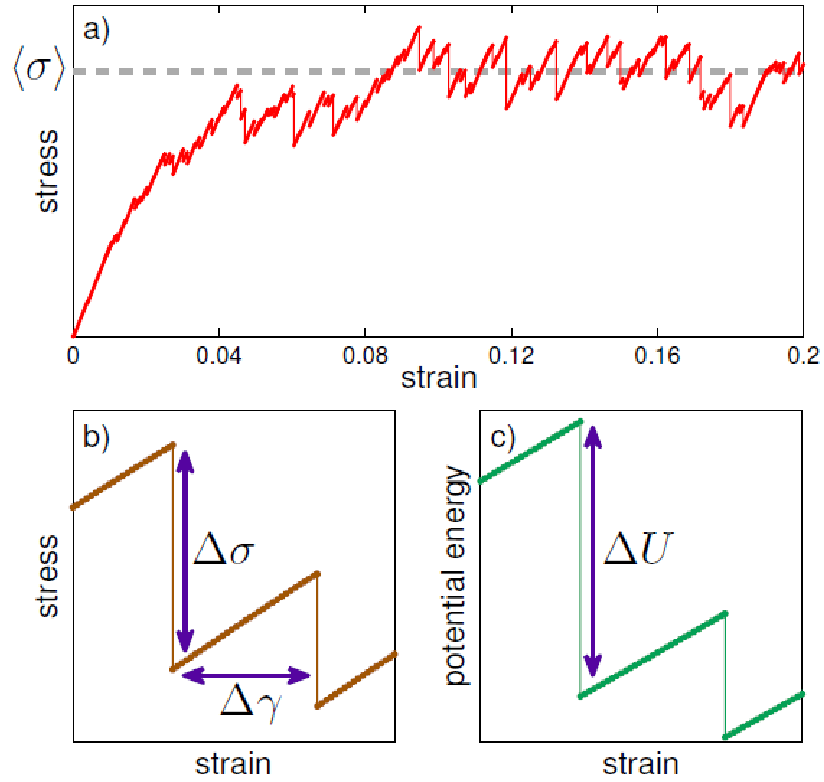
$$\dot{\mathbf{p}}_i = \mathbf{F}_i - \mathbf{p}_i \cdot \nabla \mathbf{v}\,.$$

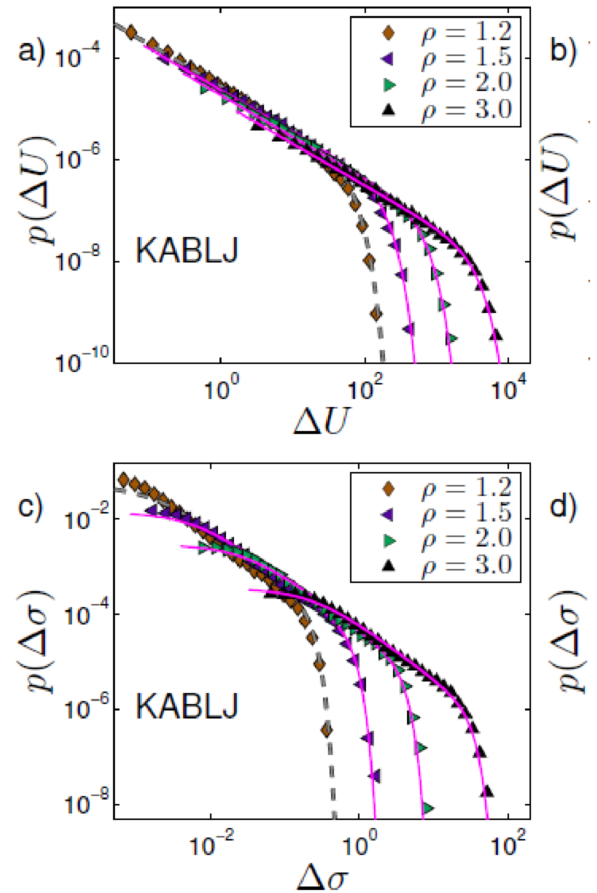
$$\frac{A\rho^4 - B\rho^2}{T} = \mathrm{Const}\,.$$



Plastic flow event statistics

[Phys. Rev. E **90**, 052304 (2014), with Edan Lerner]



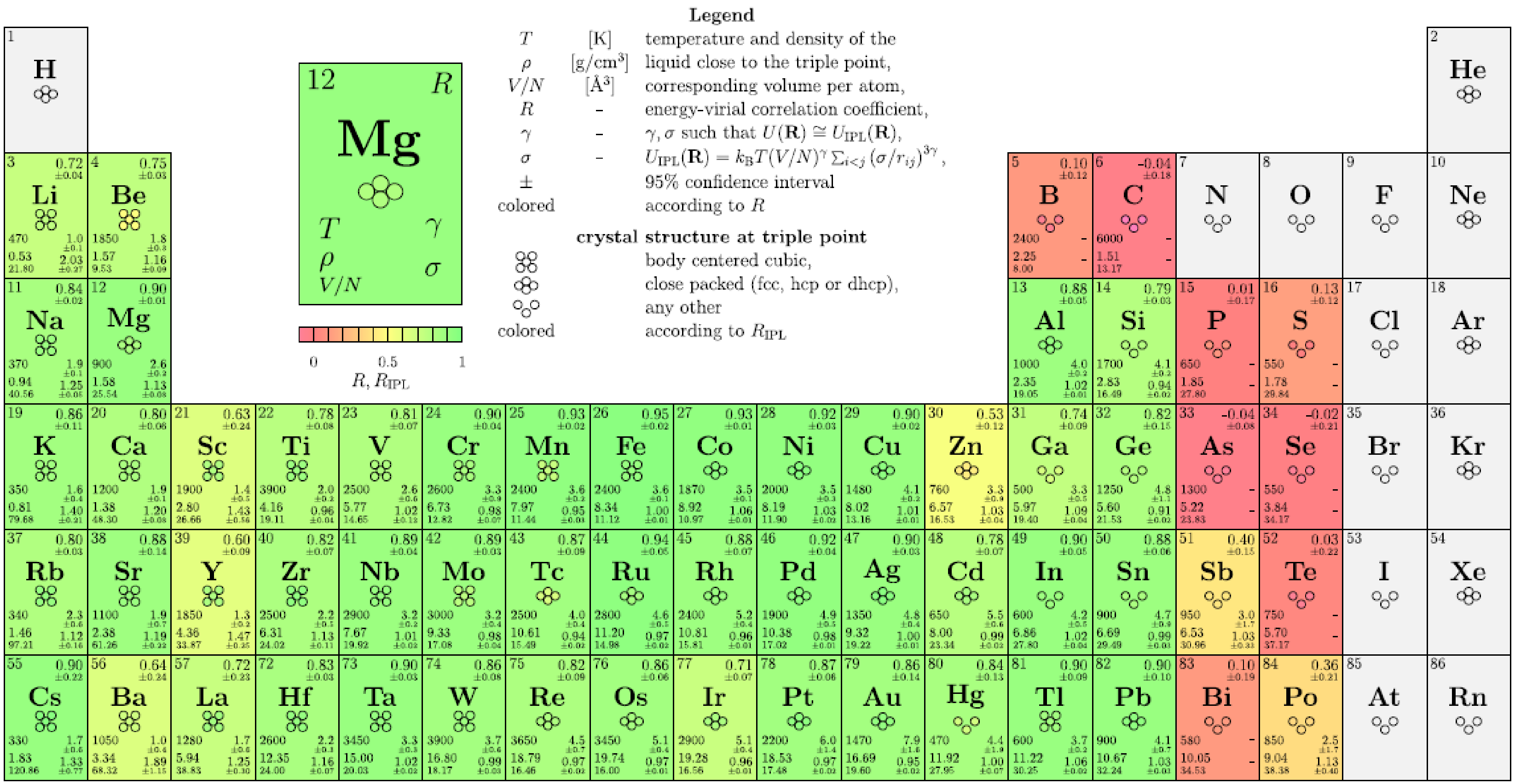


Relevant variables:

$$\Delta U/h(\rho) \text{ and } \Delta\sigma/\rho h(\rho)$$

Elements

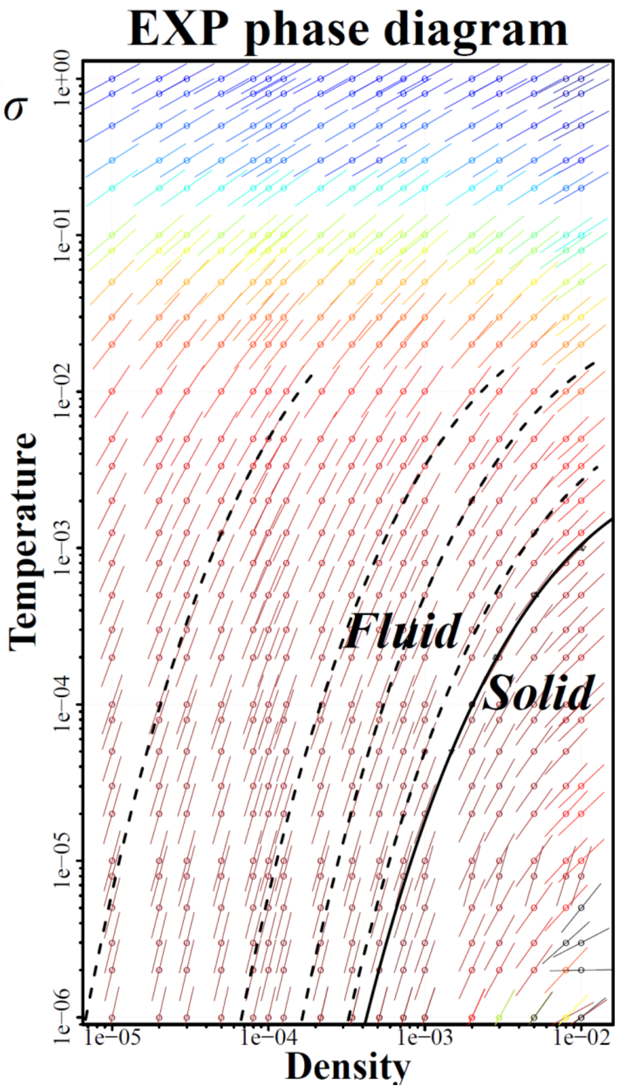
[Phys. Rev. B **92**, 174116 (2015), with Georg Kresse and Felix Hummel]

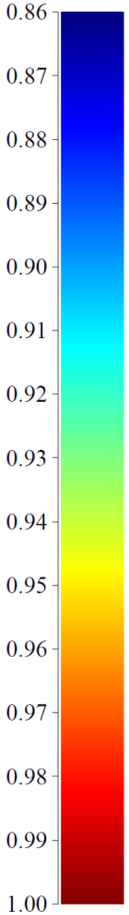


The *EXP* system

[Nat. Comm. **5**, 5424 (2014); J. Phys.: Cond. Mat. **28**, 323001 (2016)]

$$\upsilon_{\mathrm{EXP}}(r, \varepsilon, \sigma) = \varepsilon\, e^{-r/\sigma}$$





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

The *EXP* pair potential in the isomorph framework

$$v_{\mathrm{EXP}}(r,\varepsilon,\sigma) = \varepsilon\, e^{-r/\sigma}$$

$$U_{\mathrm{EXP}}(\mathbf{R}) \cong h_{\mathrm{EXP}}(\rho)\tilde{\Phi}_{\mathrm{EXP}}(\tilde{\mathbf{R}}) + g_{\mathrm{EXP}}(\rho) \qquad \tilde{\mathbf{R}} \equiv \rho^{1/3}\mathbf{R}$$

$$g_{\mathrm{EXP}}(\rho) = \varepsilon \tilde{g}_{\mathrm{EXP}}(\rho\sigma^3)$$ (same for h(rho))

<u>Implication:</u>

$$v(r) = \int_0^\infty f(\sigma) e^{-r/\sigma} d\sigma$$

$$g(\rho) \equiv \int_0^\infty f(\sigma)\tilde{g}_{\mathrm{EXP}}(\rho\sigma^3) d\sigma$$ etc

leads to:

$$U(\mathbf{R}) \cong h(\rho)\tilde{\Phi}_{\mathrm{EXP}}(\tilde{\mathbf{R}}) + g(\rho)$$

Characterization of quasiuniversal pair potentials

In terms of reduced units $\tilde{r} \equiv \rho^{1/3} r$ $\tilde{\upsilon} \equiv \upsilon / k_B T$

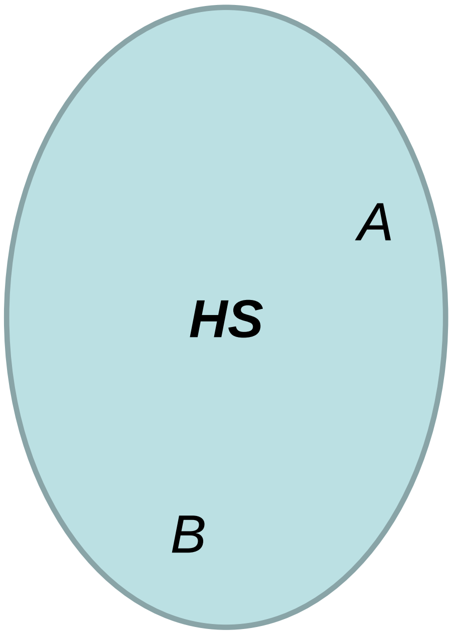
a system is quasiuniversal whenever

$$\tilde{\upsilon}(\tilde{r}) \cong \sum_j \Lambda_j e^{-u_j \tilde{r}}, \; |\Lambda_j| \gg 1$$

Examples: Inverse-power law systems (including OCP)
Lennard-Jones, Yukawa, …

Not: Lennard-Jones Gaussian model, Gaussian-core model,
Jagla potential, …

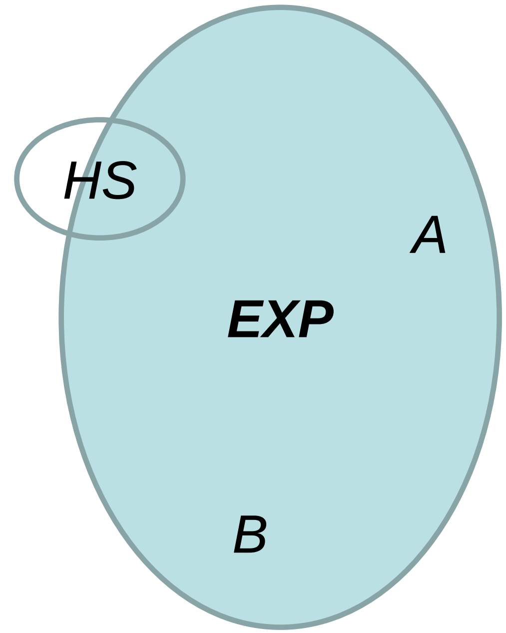
Traditional picture



$A \cong B$ because

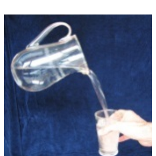
$A \cong HS$ and $B \cong HS$

Proposed picture



$A \cong B$ because

$A \cong EXP$ and $B \cong EXP$

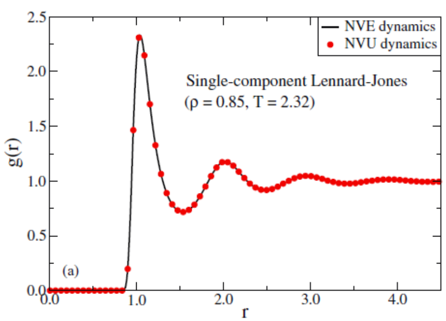


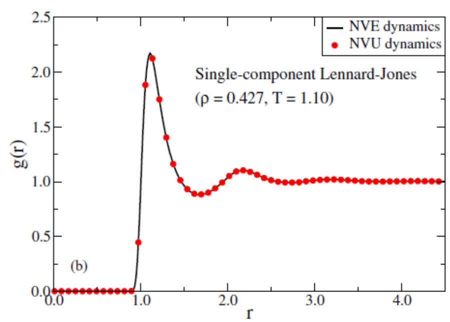
NVU dynamics:
”Replacing Newton’s second law by his first”

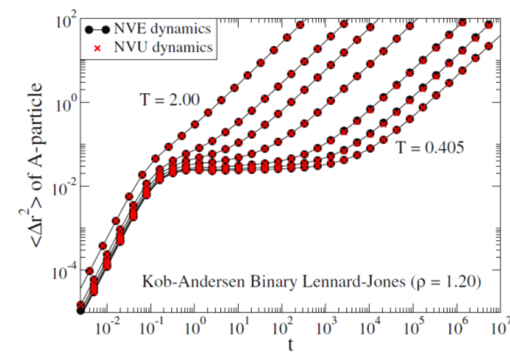
[J. Chem. Phys. **135**, 104101; 104102 (2011); **137**, 244101 (2012)]

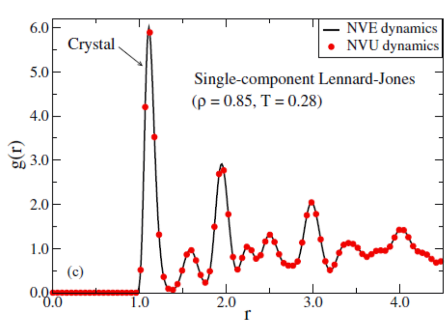
Geodesic motion on $\Omega = \{\mathbf{R} \in R^{3N} \mid U(\mathbf{R}) = U_0\}$ where $\mathbf{R} \equiv (\mathbf{r}_1, \ldots, \mathbf{r}_N)$

$$\mathbf{R}_{i+1} = 2\mathbf{R}_i - \mathbf{R}_{i-1} - 2\,\frac{\mathbf{F}_i \cdot (\mathbf{R}_i - \mathbf{R}_{i-1})}{\mathbf{F}_i^2}\mathbf{F}_i$$









Verlet algorithm:

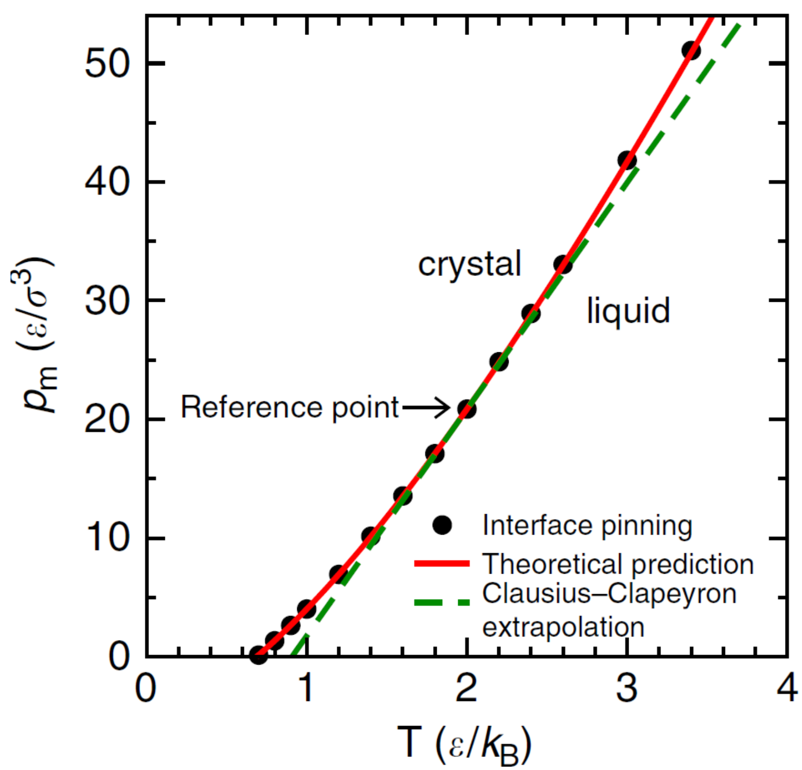
$$\mathbf{R}_{i+1} = 2\,\mathbf{R}_i - \mathbf{R}_{i-1} + \frac{(\Delta t_{NVE})^2}{m}\mathbf{F}_i$$

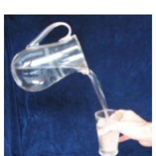
Freezing and melting of the LJ system

[Nat. Comm. **7**, 12386 (2016)]

$$p_m(T)V(T) - Nk_\mathrm{B}T - W^\mathrm{I}(T) = \left(\frac{\partial W}{\partial \ln \tilde{\rho}}\right)_T^\mathrm{I} \ln(\tilde{\rho}/\tilde{\rho}^\mathrm{I})$$

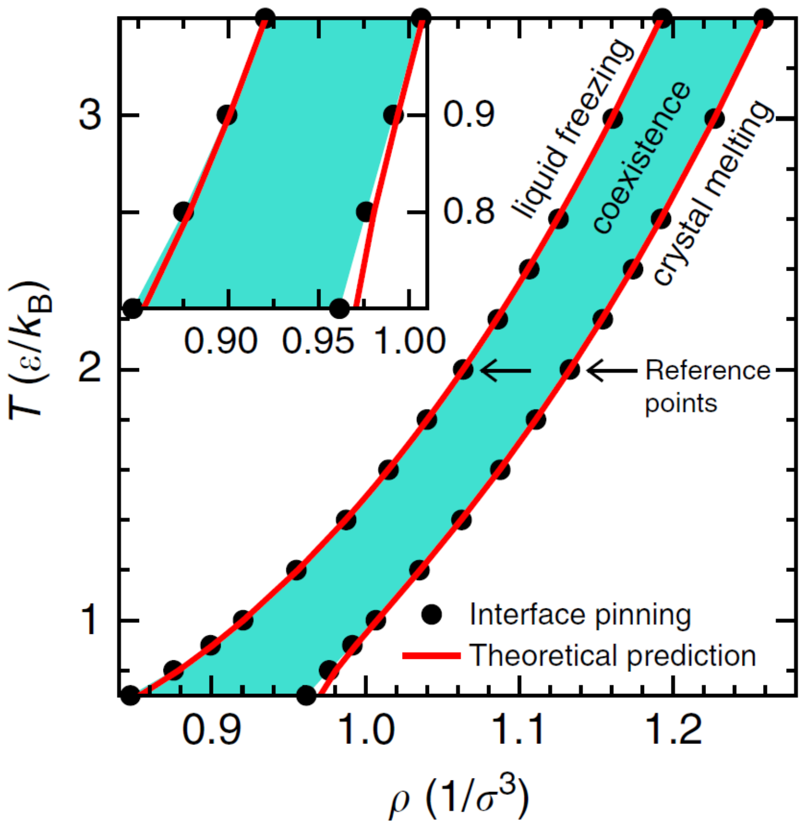
$$\left(\frac{\partial W}{\partial \ln \tilde{\rho}}\right)_T^\mathrm{I} = \left(\frac{m}{3}\right)^2 A_m(\tilde{\rho}^\mathrm{I})^{m/3} + \left(\frac{n}{3}\right)^2 A_n(\tilde{\rho}^\mathrm{I})^{n/3} - \frac{\left(\frac{m}{3}A'_m(\tilde{\rho}^\mathrm{I})^{m/3} + \frac{n}{3}A'_n(\tilde{\rho}^\mathrm{I})^{n/3}\right)^2}{A''_m(\tilde{\rho}^\mathrm{I})^{m/3} + A''_n(\tilde{\rho}^\mathrm{I})^{n/3}}$$

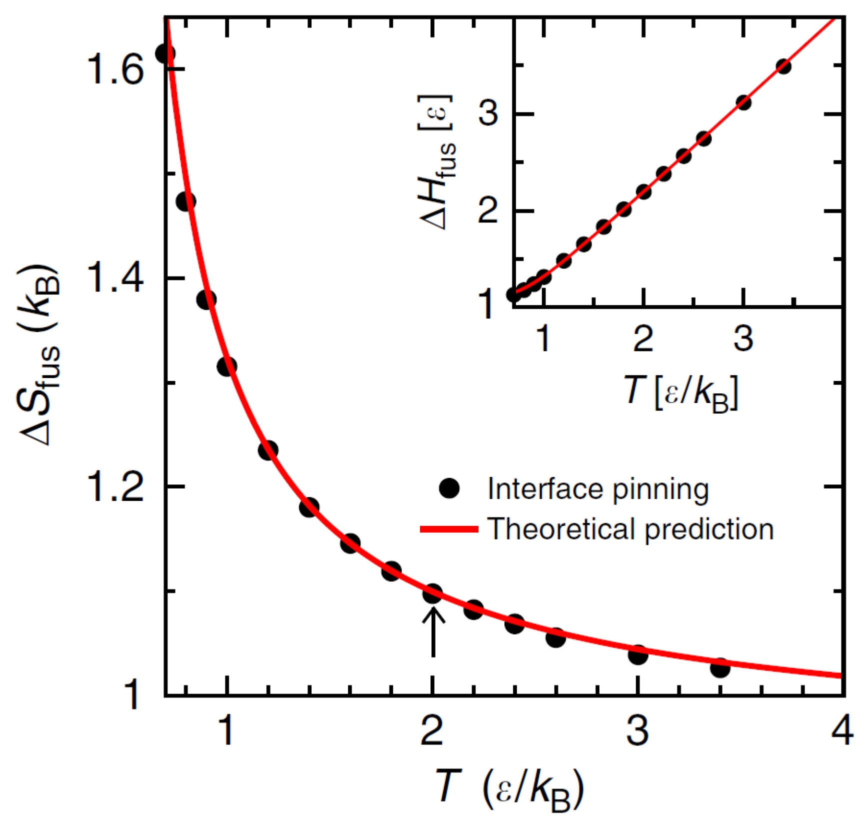




Freezing and melting of the LJ system

[Nat. Comm. **7**, 12386 (2016)]





Other works involving the isomorph concept

- Biomembranes [J. Phys. Chem. B **114**, 2124 (2010)]
- Explaining why the fictive temperature only depends on final density [Phys. Rev. Lett. **104**, 125902 (2010)]
- Flows under nanoconfinement [Phys. Rev. Lett. **111**, 235901 (2013)]
- Arguing that repulsive and attractive forces do not play separate roles for the physics [J. Phys.: Cond. Matt. **25**, 032101 (2013)]
- Yukawa pair potetial [Phys. Plasmas **22**, 073705 (2015)]
- Lennard-Jones fluid in four dimensions [J. Chem. Phys. **144**, 231101 (2016)]
- **The theory is exact in infinite dimension** [Maimbourg and Kurchan, EPL **114**, 6002 (2016)]

Summary

In realistic systems/models isomorph invariance is not exact.
Nevertheless:

- The isomorph concept provides a simplification by making parts of the phase diagram basically one-dimensional.
- Allows for saving computer/experimental time.
- The class of R-simple systems is quite large.
- Any universal theory for structure and/or dynamics of condensed matter must be isomorph invariant.

Reviews:
J. Non-Cryst. Solids **357**, 320 (2011)
Phys. Rev. X **2**, 011011 (2012)
J. Phys. Chem. B **118**, 10007 (2014)
J. Phys.: Cond. Mat. **28**, 323001 (2016)

Thanks!