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

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## "Hidden" scale invariance: Isomorph theory v2 (2014)



#### Isomorph theory, v2 [J. Chem. Phys. 141, 204502 (2014)]





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:  $S_{\text{ex}}(\mathbf{R}) \equiv S_{\text{ex}}(\rho, U(\mathbf{R}))$ 

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

$$S_{\text{ex}}(\mathbf{R}_1)/k_B = -N\ln N + \ln\left(\operatorname{Vol}\{\tilde{\mathbf{R}}' \mid U(\rho_1^{-1/3}\tilde{\mathbf{R}}') < U(\mathbf{R}_1)\}\right)$$
$$S_{\text{ex}}(\mathbf{R}_2)/k_B = -N\ln N + \ln\left(\operatorname{Vol}\{\tilde{\mathbf{R}}' \mid U(\rho_2^{-1/3}\tilde{\mathbf{R}}') < U(\mathbf{R}_2)\}\right)$$

Applying  $\lambda=
ho_2^{-1/3}
ho_1^{1/3}$  leads to identity, i.e. (  $ilde{f R}\equiv
ho^{1/3}{f R}$  )

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



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

1) Invariant structure and dynamics along the configurational adiabats

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

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

2) Invariant Boltzmann probabilities along the configurational adiabats  $U(\mathbf{R}) \cong U + T(\rho, S_{ex}) \left(S_{ex}(\tilde{\mathbf{R}}) - S_{ex}\right)$ 

Two configurations on config. adiabat with same reduced coordinates obey  $U(\mathbf{R}_1) - U_1 = U(\mathbf{R}_2) - U_2$ 



$$\frac{U(\mathbf{R}_{1}) - U_{1}}{k_{B}T_{1}} \cong \frac{U(\mathbf{R}_{2}) - U_{2}}{k_{B}T_{2}}$$
$$\exp(-U(\mathbf{R}_{1})/k_{B}T_{1}) \cong C_{12}\exp(-U(\mathbf{R}_{2})/k_{B}T_{2})$$

## "Hidden scale invariance"

R-simple systems obey

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

This class includes most:

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

This class excludes most:

- 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]

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

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

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





#### Plastic flow event statistics [Phys. Rev. E 90, 052304 (2014), with Edan Lerner]







 $\Delta U/h(\rho)$  and  $\Delta \sigma/\rho h(\rho)$ 



## Elements

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

				Legena				
1	7		T	[K] temperature a	and density of the			2
н		10	ρ [g	[/cm <sup>3</sup> ] liquid close to	the triple point,			He
- <del>-</del>		12	R V/N	[Å <sup>3</sup> ] corresponding	g volume per atom,			110
-00			R	<ul> <li>energy-virial e</li> </ul>	correlation coefficient,			
		Μσ	• γ	<ul> <li>- γ, σ such that</li> </ul>	$U(\mathbf{R}) \cong U_{\mathrm{IPL}}(\mathbf{R}),$			
3 0.72	2 4 0.75		σ	$ U_{IPL}(\mathbf{R}) = k_B$	$T(V/N)^{\gamma} \sum_{i < j} (\sigma/r_{ij})^{3\gamma}$ ,	5 0.10 6 -0.0	4 7 8	9 10
±0.04	±0.03		±	95% confidence	ce interval	<b>D</b> <sup>±0.12</sup>		D N
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±0.02	12 0.50 ±0.01	• / • •	 0_0	any other	(ree, nop or anop),	10 0.00 14 0.1 ±0.05 ±0.	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	11 10
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40.56 ±0.05	5 25.54 ±0.08	re, reiPL				19.05 +0.01 16.49 +0	02 27.80 29.84	
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${f K}^{19}{f K}^{0.86}$	$\mathbf{\hat{L}}^{20}$ 0.80 $\overset{0.80}{\pm 0.06}$ $\overset{21}{\mathbf{Sc}}$ 0.63 $\overset{0.63}{\pm 0.24}$	${\stackrel{22}{\overset{0.78}{_{\pm 0.08}}}{ m Ti}}{\stackrel{23}{_{\pm 0.07}}}{ m V}^{0.81}$	${f Cr}^{24} {f O.90}_{\pm 0.04} {f Z5} {f O.93}_{\pm 0.02} {f Mn}$	${f Fe}^{26} {f O.95}_{\pm 0.02} {f Z7}^{27} {f O.93}_{\pm 0.01} {f Co}^{0.93}$	$\overset{28}{\overset{0.92}{\overset{\pm 0.03}{\overset{\pm 0.03}{\overset{\pm 0.02}{\overset{\pm 0.02}}{\overset{\pm 0.02}{\overset{\pm 0.02}{\overset{\pm 0.02}{\overset{\pm 0.02}$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	${}^{32}_{15} {}^{33} {}^{-0.04}_{\pm 0.08} {}^{34}_{\pm 0.21} {}^{-0.02}_{\pm 0.21} {}^{33}_{{}^{\pm 0.21}} {}^{33}_{{}^{\pm 0.21}}$	<sup>35</sup> Br Kr
19 0.86 ±0.11 <b>K</b>	${f L}^{20} = {f 0.80}_{\pm 0.06} {f 21} = {f 0.63}_{\pm 0.24} {f 0.63}_{\pm 0.24} {f Ca} {f Sc}_{88} {f 0.86}_{88} {f 0.8$	${ \begin{array}{cccc} & 0.78 \\ \pm 0.08 \\ {f Ti} \\ 88 \end{array} } { \begin{array}{c} 23 & 0.81 \\ \pm 0.07 \\ {f V} \\ 88 \end{array} } { f V} $	${egin{array}{c c} & 24 & 0.90 \\ & \pm 0.04 \\ & \mathbf{Cr} \\ & 88 \\ & 88 \\ & 88 \end{array}} {egin{array}{c c} & 25 & 0.93 \\ \pm 0.02 \\ & \pm 0.02 \\ &$	${f Fe}_{{\otimes}{\otimes}{\otimes}{\otimes}{\otimes}{\otimes}{\otimes}{\otimes}{\otimes}{\otimes}{\otimes}{\otimes}{\otimes}$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	${f As}_{0,0}^{33} = {f 0.04}_{\pm 0.08}^{34} {f 34}_{\pm 0.21}^{-0.02} {f Se}_{\pm 0.21}^{-0.02}$	$\begin{array}{ccc} 35 & 36 \\ \mathbf{Br} & \mathbf{Kr} \\ \circ_{0} \circ & \infty \end{array}$
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$ \begin{smallmatrix} 19 & 0.86 \\ \pm 0.11 \\ K \\ 000 \\ 350 & \pm 0.4 \\ 0.81 & \pm 0.4 \\ 37 & 0.80 \\ 37 & 0.80 \\ \end{smallmatrix} $	$\begin{smallmatrix} 1 & 20 & 0.80 \\ \pm 0.06 \\ \hline \\ 1 & 20 \\ \hline \\ 1 & 20 \\ 1 & 30 \\ 1.38 \\ 1.38 \\ 1.20 \\ 1.38 \\ 1$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	35 Br ₀₀○ 53 54
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## The EXP system

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



# The EXP pair potential in the isomorph framework $\int_{1}^{1} \frac{1}{2} dx$

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

leads to:

$$U_{\text{EXP}}(\mathbf{R}) \cong h_{\text{EXP}}(\rho) \tilde{\Phi}_{\text{EXP}}(\tilde{\mathbf{R}}) + g_{\text{EXP}}(\rho) \qquad \tilde{\mathbf{R}} \equiv \rho^{1/3} \mathbf{R}$$
  
 $g_{\text{EXP}}(\rho) = \varepsilon \tilde{g}_{\text{EXP}}(\rho \sigma^3) \qquad \text{(same for h(rho))}$ 

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

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

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



## Characterization of quasiuniversal pair potentials

In terms of reduced units  $ilde{r}\equiv
ho^{1/3}r$   $ilde{v}\equiv v/k_BT$ 

a system is quasiuniversal whenever

$$\tilde{v}(\tilde{r}) \cong \sum_{j} \Lambda_{j} e^{-u_{j}\tilde{r}}, |\Lambda_{j}| \gg 1$$

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

<u>Not</u>: Lennard-Jones Gaussian model, Gaussian-core model, Jagla potential, ...





## *NVU* dynamics: "Replacing Newton's second law by his first"

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

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

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



## Freezing and melting of the LJ system

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

$$p_{m}(T)V(T) - Nk_{\rm B}T - W^{\rm I}(T) = \left(\frac{\partial W}{\partial \ln \tilde{\rho}}\right)_{T}^{\rm I} \ln(\tilde{\rho}/\tilde{\rho}^{\rm I}) \\ \left(\frac{\partial W}{\partial \ln \tilde{\rho}}\right)_{T}^{\rm I} = \left(\frac{m}{3}\right)^{2} A_{m}(\tilde{\rho}^{\rm I})^{m/3} + \left(\frac{n}{3}\right)^{2} A_{n}(\tilde{\rho}^{\rm I})^{n/3} - \frac{\left(\frac{m}{3}A'_{m}(\tilde{\rho}^{\rm I})^{m/3} + \frac{n}{3}A'_{n}(\tilde{\rho}^{\rm I})^{n/3}\right)^{2}}{A''_{m}(\tilde{\rho}^{\rm I})^{m/3} + A''_{n}(\tilde{\rho}^{\rm I})^{n/3}}$$



19



## 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!

