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The mother of all pair potentials

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Abstract This paper presents a computer simulation study of the exponentially repulsive pair potential system. The simulations show that the system has strong virial potential energy correlations in a large part of its thermodynamic phase diagram. Consequences of this are briefly discussed; these include the existence of isomorphs and predictions for general simple liquids and solids.

Keywords Simple liquids · Simple solids · Exponential pair potential

Introduction

The first Gulf war was triggered by Iraq's occupation of Kuwait in 1990. When the Americans and their allies counterattacked in 1991, Saddam Hussein spoke of the “mother of all wars.” War is a terrible thing, and hopefully, we shall never experience any mother of all wars. This paper is devoted to peace and prosperity for Friedrich Kremer, his family, and many friends; his numerous important scientific contributions dealing with simple as well as quite complex systems have been a great source of inspiration for a large scientific community.

Following up on a brief remark made in Ref. [5], this paper argues that the simple exponentially repulsive pair potential—denoted by EXP –

$$v_{\text{EXP}}(r; \varepsilon, \sigma) = \varepsilon e^{-r/\sigma} \quad (1)$$

deserves to be referred to as the “mother of all pair potentials.” By this is meant that the EXP pair potential can be regarded as a building block of any general, analytical pair potential.

The paper first briefly reviews the theory of isomorphs in “[The theory of isomorphs](#),” which forms the background and motivation for the computer simulations. We then show from simulations that the EXP pair potential system has strong virial potential energy correlations [12] (“[Results from computer simulations of the EXP pair potential](#)”). The paper concludes in “[Discussion](#)” by briefly discussing the consequences of this.

The theory of isomorphs

An isomorph is a curve in the thermodynamic phase diagram along which a number of properties are invariant. Much of the evidences for the existence of isomorphs come from computer simulations. Based on these, as well as on experimental facts, we believe the following systems have isomorphs in their condensed phases: most or all van der Waals-bonded systems, metals and systems with weak ionic and/or dipolar interactions. Systems without isomorphs include most or all hydrogen-bonded systems, covalently bonded systems, and systems with strongly ionic and/or dipolar interactions. Thus, roughly half of all systems are conjectured to have isomorphs. Although the isomorph theory was developed for liquids [9], it was recently shown to work even better for crystals [2]. No realistic system has isomorphs throughout its entire thermodynamic phase diagram; the theory is limited to “ordinary” liquid or solid condensed matter; in particular, it always breaks down close to the critical point and in the gas phase.

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The isomorph theory has been reviewed recently in Refs. [11, 13, and in Dyre (2014) Hidden scale invariance in condensed matter. submitted to J Phys Chem B] to which the reader is referred for details. Here, we limit ourselves to summarizing the points needed to understand the simulations.

An isomorph is a curve in the thermodynamic phase diagram defined as the equivalence class of the following equivalence relation: Two state points with density (i.e., number of particles divided by the volume) and temperature (ρ_1, T_1) and (ρ_2, T_2) , respectively, are equivalent if pairs of configurations from each of the state points, which scale uniformly into one another, have the same canonical probability. If the potential energy as a function of all particle coordinates $\mathbf{R} \equiv (\mathbf{r}_1, \dots, \mathbf{r}_N)$ is denoted by $U(\mathbf{R})$, this translates into the condition [9]

$$\exp \left[-U(\rho_1^{-1/3} \tilde{\mathbf{R}}) / k_B T_1 \right] = C_{12} \exp \left[-U(\rho_2^{-1/3} \tilde{\mathbf{R}}) / k_B T_2 \right] \quad (2)$$

in which $\tilde{\mathbf{R}} \equiv \rho^{1/3} \mathbf{R}$ is the so-called reduced coordinate of the configuration \mathbf{R} at density ρ . The value of the constant C_{12} , which depends on the state points but not on the two configurations, is irrelevant for (much of) the statistical mechanics at the two state points because when the probabilities are normalized, Eq. (2) implies identical probabilities of scaled configurations, independent of the value of C_{12} .

The isomorph concept is only approximate—we do not require exact equality in Eq. (2) nor do we require that Eq. (2) is obeyed for all configurations as long as it applies for all the physically relevant ones [9]. Along an isomorph structure and dynamics are invariant when given in the so-called reduced units defined by the energy unit $k_B T$, length unit $\rho^{-1/3}$, and time unit $\rho^{-1/3} \sqrt{m/k_B T}$ where m is the particle mass. Moreover, the isochoric heat capacity and the excess entropy S_{ex} (the entropy minus that of an ideal gas at same density and temperature) are isomorph invariants.

In computer simulations, an isomorph is identified by making use of the following general, statistical-mechanical relation for the so-called density-scaling exponent γ (in which W is the virial defined by $W(\mathbf{R}) \equiv -1/3 \mathbf{R} \cdot \nabla U(\mathbf{R})$, which gives the contribution to the pressure times volume from the interactions),

$$\gamma \equiv \left(\frac{\partial \ln T}{\partial \ln \rho} \right)_{S_{\text{ex}}} = \frac{\langle \Delta W \Delta U \rangle}{\langle (\Delta U)^2 \rangle}. \quad (3)$$

The averages on the right-hand side are NVT canonical averages that are easily calculated from an equilibrium simulation at a given state point. To trace out an isomorph in the thermodynamic phase diagram, one proceeds as follows. From an initial state point, density is changed slightly, for instance, by 1 %. Then, temperature is changed by $\gamma\%$ in

order to have constant S_{ex} , i.e., to stay on the isomorph. After equilibration at the new state point, a new γ is calculated, etc. In this way, the isomorph is traced out step by step. For small density changes γ may be regarded as constant, and integration of Eq. (3) tells us that isomorphs are given by $\rho^\gamma / T = \text{Const}$. This is the so-called power-law density-scaling relation [7, 14]. In experiments on viscous, glass-forming liquids, one makes use of the fact that the reduced relaxation time is isomorph invariant and identifies an isomorph with an isochrone (these are systems for which the difference between reduced and actual relaxation time is insignificant).

As mentioned, not all systems have isomorphs. How to identify which systems have good isomorphs? A convenient test checks for virial potential-energy correlations in the NVT thermal-equilibrium fluctuations. If these are strong—typically quantified by requiring the Pearson correlation coefficient to be larger than 0.9—the system has good isomorphs and vice versa (Appendix A of Ref. [9]).

We originally called systems with isomorphs and strong virial potential energy correlations for “strongly correlating liquids,” but that term kept being confused with “strongly correlated quantum systems.” Systems with isomorphs have simple properties, so a good name would be “simple systems.” However, the term “simple liquid” is already defined and used 50 years ago as a system of particles interacting via pairwise additive forces. As a consequence, systems with isomorphs are now referred to as “Roskilde-simple systems” or just “Roskilde systems” [6, 11].

The most concise formulation of the isomorph theory is based on the following recently derived “hidden scale invariance” identity [4]

$$U(\mathbf{R}) \cong h(\rho) \tilde{\Phi}(\tilde{\mathbf{R}}) + g(\rho). \quad (4)$$

Here, $\tilde{\Phi}(\tilde{\mathbf{R}})$ is a dimensionless function of the dimensionless configuration variable $\tilde{\mathbf{R}}$, which in particular involves neither the characteristic energy of the potential ε nor its characteristic length σ . Since all of structure and dynamics are contained in this function, systems obeying Eq. (4) are scale invariant. Equation (4) states that upon a change of density, the only thing that happens to the potential energy surface is an overall linear affine scaling. The function $h(\rho)$ gives the density-dependent scaling of the potential energy surface (which is compensated along an isomorph since $T \propto h(\rho)$). The function $g(\rho)$ gives the “vertical” displacement of the potential energies, which has no influence on the dynamics and only influences the free energy and the so-called cold pressure.

The connection to the isomorph theory is that a system has good isomorphs—is Roskilde simple—if and only if it obeys Eq. (4). In fact, the properties of such systems are all easily derived from Eq. (4) (see the recent paper Ref.

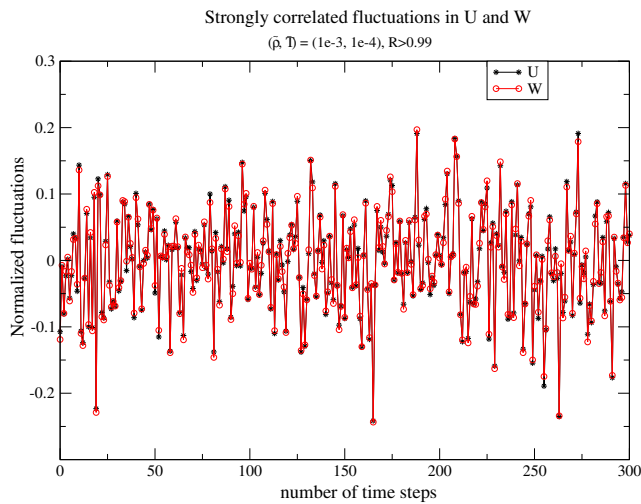


Fig. 1 Fluctuations in the potential energy and the virial of the EXP system over 300 time steps of a computer simulation of the state point $(\tilde{\rho}, \tilde{T}) = (10^{-3}, 10^{-4})$ at which $R > 0.99$ ($\tilde{\rho} \equiv \rho\sigma^3$ and $\tilde{T} \equiv k_B T/\varepsilon$). The fluctuations of both potential energy and virial are calculated as derivations from the mean. In order to allow for an easy comparison to the virial fluctuations, the fluctuations in potential energy were rescaled by multiplying with the standard deviation of W and dividing by the standard deviation of U

[4]). The many simple properties of Roskilde-simple liquids have been detailed in previous publications, e.g., Refs. [9–11], and will not be repeated here. A much less studied fact is that crystalline solids also can have isomorphs;

in fact, the predicted isomorph invariants appear to apply better for solids than for liquids [2]. In this regard, it is interesting to note that the melting line itself is an isomorph, a fact that explains the several invariants that have been reported along this line, e.g., the excess entropy, the reduced viscosity, the pair distribution function, etc. (see Ref. [5] and its references). For instance [5, 9], the isomorph theory is consistent with the famous Lindemann melting criterion and its pressure independence, the criterion according to which melting takes place when the atoms' thermal vibration amplitude upon heating reaches a certain fraction of the nearest-neighbor distance [8, 15].

Results from computer simulations of the EXP pair potential

We simulated 1,000 particles interacting via the EXP pair potential at several thermodynamic state points in order to investigate whether there are strong correlations in the thermal equilibrium constant-volume fluctuations of virial and potential energy. The simulations used the Roskilde University Molecular Dynamics (RUMD) code for GPU computing [1] and were all carried out in the standard NVT ensemble with a Nose-Hoover thermostat with a time step of 0.0025 in LJ units. A shifted forces' cutoff at $r = 2\rho^{-1/3}$ was used throughout, which is

Table 1 Table of virial potential-energy correlation coefficients for low-density low-temperature state points of the EXP system

		Temperature (\tilde{T}) $\cdot 10^{-3}$									
		0.05	0.1	0.2	0.3	0.5	0.8	1.25	2.00	3.33	10.0
Density ($\tilde{\rho}$) $\cdot 10^{-3}$	0.13	0.996	0.996	0.995	0.994	0.993	0.992	0.991	0.989	0.988	0.981
	0.22	0.996	0.996	0.995	0.994	0.993	0.992	0.991	0.990	0.988	0.981
	0.34	0.997	0.996	0.995	0.994	0.993	0.992	0.991	0.990	0.988	0.981
	0.51	0.997	0.996	0.995	0.995	0.994	0.993	0.991	0.990	0.988	0.981
	0.73	0.997	0.996	0.995	0.995	0.994	0.993	0.992	0.990	0.988	0.981
	1.00	0.997	0.997	0.996	0.995	0.994	0.993	0.992	0.990	0.988	0.981
	1.33	0.998	0.997	0.996	0.995	0.994	0.993	0.992	0.990	0.988	0.980
	1.73	0.998	0.997	0.996	0.995	0.994	0.993	0.992	0.990	0.988	0.981
	2.20	0.998	0.997	0.996	0.996	0.994	0.993	0.992	0.990	0.988	0.980
	2.74	0.997	0.997	0.996	0.996	0.994	0.993	0.992	0.990	0.988	0.980
	3.37	0.997	0.997	1.000	0.995	0.994	0.993	0.992	0.990	0.987	0.979
	4.10	0.992	0.996	0.996	0.995	0.994	0.993	0.992	0.990	0.987	0.978
	4.91	0.964	0.992	0.996	0.995	0.993	0.992	0.991	0.989	0.986	0.977
	5.83	0.980	0.988	0.994	0.993	0.993	0.992	0.990	0.988	0.985	0.976
	6.86	0.949	0.988	0.991	0.991	0.993	0.991	0.989	0.987	0.984	0.974
	8.00	0.917	0.960	0.984	0.986	0.992	0.989	0.988	0.986	0.983	0.972

We see that this system obeys the requirement of strong virial potential-energy correlations $R > 0.9$ [9, 12] whenever $k_B T \ll \varepsilon$ and $\rho\sigma^3 \ll 1$

considerably larger than the decay length of the EXP function σ in the region of the thermodynamic phase diagram the simulations focused on, the low-density region where $\rho\sigma^3 \ll 1$.

At each state point, we evaluated the virial potential-energy correlation coefficient R defined by

$$R \equiv \frac{\langle \Delta U \Delta W \rangle}{\sqrt{\langle (\Delta U)^2 \rangle \langle (\Delta W)^2 \rangle}}. \quad (5)$$

Figure 1 shows a typical snapshot of the the fluctuations of virial (red) and potential energy (black) as functions of time at the state point defined by $\rho\sigma^3 = 10^{-3}$ and $k_B T/\varepsilon = 10^{-4}$. In the figure, the potential energy was rescaled to allow for a comparison to the virial fluctuations. We see that these two quantities correlate strongly, in fact, $R > 99\%$ at this state point.

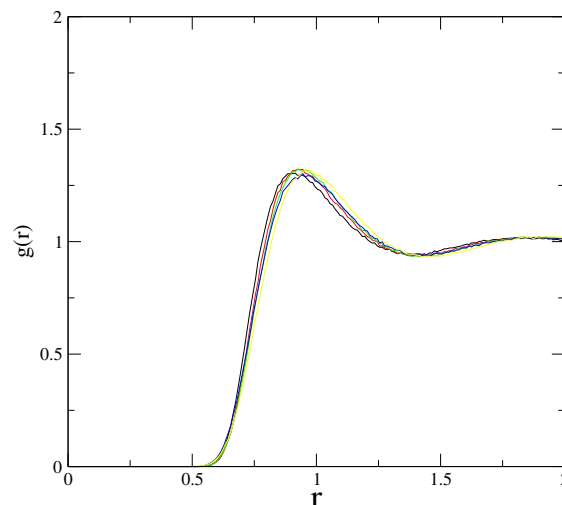
Table 1 shows our simulation results for R at several low-density, low-temperature state points. It is clear that the EXP system has strong virial potential energy correlations in the part of its phase diagram where $\rho\sigma^3 \ll 1$ and $k_B T/\varepsilon \ll 1$, which is the focus here. Actually, the criterion $R > 0.9$ previously used as defining the class of “strongly correlating” Roskilde liquids is well obeyed. According to the isomorph theory, this implies the existence of good isomorphs [9]. In order to verify this, we identified a few state points that are approximately isomorphic. Figure 2a shows the resulting radial distribution functions in reduced units, and Fig. 2b shows the mean square displacement as a function of time for the same state points, also in reduced units. We conclude that isomorph invariance is obeyed to a good approximation.

Discussion

This paper has shown that the EXP pair potential is Roskilde simple in the low-density, low-temperature part of the thermodynamic phase diagram, i.e., has strong correlations between its thermal equilibrium fluctuations of virial and potential energy.

It is possible to expand an analytical pair potential in terms of inverse power law (IPL) functions. If $v(r) = \varepsilon \sum_n v_n (r/\sigma)^{-n}$, one finds because each $(r/\sigma)^{-n}$ term may itself be written as a sum of EXP functions that in Eq. (4), $h(\rho) \equiv \varepsilon \sum_n v_n \alpha_n (\rho\sigma^3)^{n/3}$ and $g(\rho) \equiv \varepsilon \sum_n v_n \beta_n (\rho\sigma^3)^{n/3}$ for some constants α_n and β_n . We conclude that the EXP pair-potential system—by having strong virial potential-energy correlations and being a building block of analytical pair potentials—has the properties which may justify naming it the “mother of all pair potentials.”

Radial distribution function



Mean square displacement

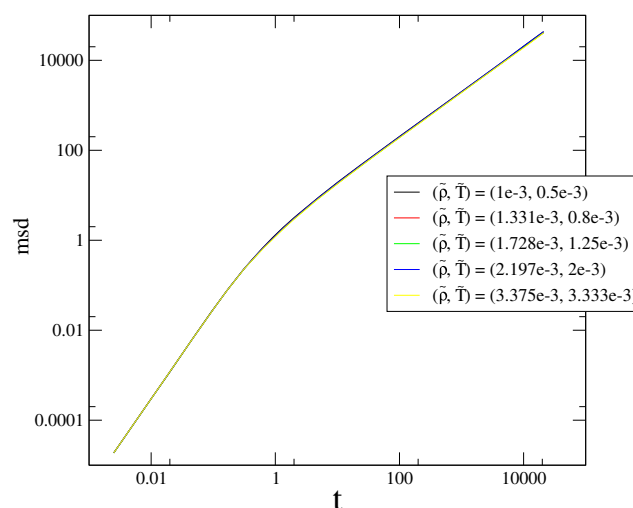


Fig. 2 **a** Radial distribution functions and **b** mean square displacement as a function of time, both in reduced units, along an isomorph, demonstrating isomorph invariance

In hindsight, it may seem puzzling that the EXP pair potential never became one of the standard pair potentials used in numerical studies. The reason is probably that purely repulsive pair potentials were always considered to be unphysical because they have no liquid “bound state” of negative potential energy and, consequently, no liquid-gas phase transition. The isomorph theory questions this paradigm, however, by having no need to distinguish sharply between potentials with and without bound states. The theory, incidentally, also questions the standard liquid-state paradigm that repulsive and attractive forces play distinct roles for the physics of liquids. For a more detailed discussion of this, the reader is referred to Ref. [3].

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Andreas K. Bacher High-school teacher in physics and mathematics; the paper is based on his master’s thesis.



Jeppe C. Dyre Professor of Physics at Roskilde University and director of the DNRF center *Glass and Time*. JCD has known Friedrich Kremer for almost 25 years. We met at a series of small workshops in Poland on dielectric phenomena, organized by the late Andrew Jonscher and coworkers just after the fall of the Berlin wall. At these meetings we quickly realized that we share many views on scientific and other matters.