

Scaling Properties of Liquid Dynamics Predicted from a Single Configuration: Pseudoisomorphs for Harmonic-Bonded Molecules

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Cite This: *J. Phys. Chem. B* 2024, 128, 8054–8064

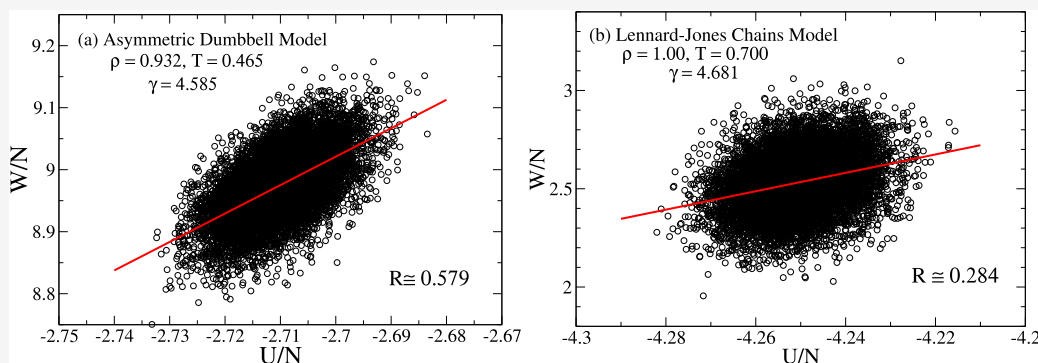


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ABSTRACT: Isomorphs are curves in the thermodynamic phase diagram of invariant excess entropy, structure, and dynamics, while pseudoisomorphs are curves of invariant structure and dynamics, but not of the excess entropy. The latter curves have been shown to exist in molecular models with flexible bonds [Olsen, A. E. et al. *J. Chem. Phys.* 2016, 145, 241103]. We here present three force-based methods to trace out pseudoisomorphs based on a single configuration and test them on the asymmetric dumbbell and 10-bead Lennard-Jones chain models with bonds modeled as harmonic springs. The three methods are based on requiring that particle forces, center-of-mass forces, and torques, respectively, are invariant in reduced units. For each of the two investigated models we identify a method that works well for tracing out pseudoisomorphs, but these methods are not the same. Overall, we find that the more internal degrees of freedom there are in the molecule studied, the less they appear to affect the gross dynamical behavior. Moreover, the “internal” degrees of freedom (including rotation) do not significantly affect the scaling behavior of the dynamical/transport coefficients provided some ‘quenching’ is performed.

1. INTRODUCTION

Isomorphs are curves of constant excess entropy in the thermodynamic phase diagram along which structure and dynamics are invariant to a good approximation.¹ We remind that the excess entropy S_{ex} is the entropy minus that of an ideal gas at the same density and temperature.² Systems with isomorphs, termed R -simple,^{3–9} are characterized by a strong correlation between the canonical-ensemble equilibrium fluctuations of potential energy U and virial W , as quantified by the Pearson correlation coefficient (sharp brackets denote canonical averages and Δ the deviation from the mean)

$$R = \frac{\langle \Delta W \Delta U \rangle}{\sqrt{\langle (\Delta W)^2 \rangle \langle (\Delta U)^2 \rangle}} \quad (1)$$

The criterion for being R -simple is $R > 0.9$,¹ but even systems with somewhat lower R values may have good isomorphs.¹⁰

Isomorph invariance of structure and dynamics refers to the use of units where the energy unit is $e_0 \equiv k_B T$, the length unit is $l_0 \equiv \rho^{-1/3}$ in which ρ is the particle number density, i.e., the

density of atoms, and the time unit is $t_0 \equiv \rho^{-1/3} \sqrt{m/k_B T}$ in which m is a particle mass. Quantities made dimensionless by reference to this unit system are termed “reduced” and marked by a tilde; for instance the reduced particle position \mathbf{r} is given by $\tilde{\mathbf{r}} \equiv \mathbf{r}/l_0 = \rho^{1/3} \mathbf{r}$.

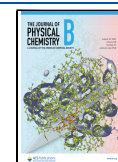
The existence of isomorphs for a given system means that the thermodynamic phase diagram is essentially one-dimensional in regard to structure and dynamics. If one imagines filming how the molecules move, two state points on the same isomorph would give rise to (almost) the same movie—except for an overall scaling of space and time. This provides an significant simplification of the physics, basically implying that

Received: June 15, 2024

Revised: July 30, 2024

Accepted: July 31, 2024

Published: August 7, 2024



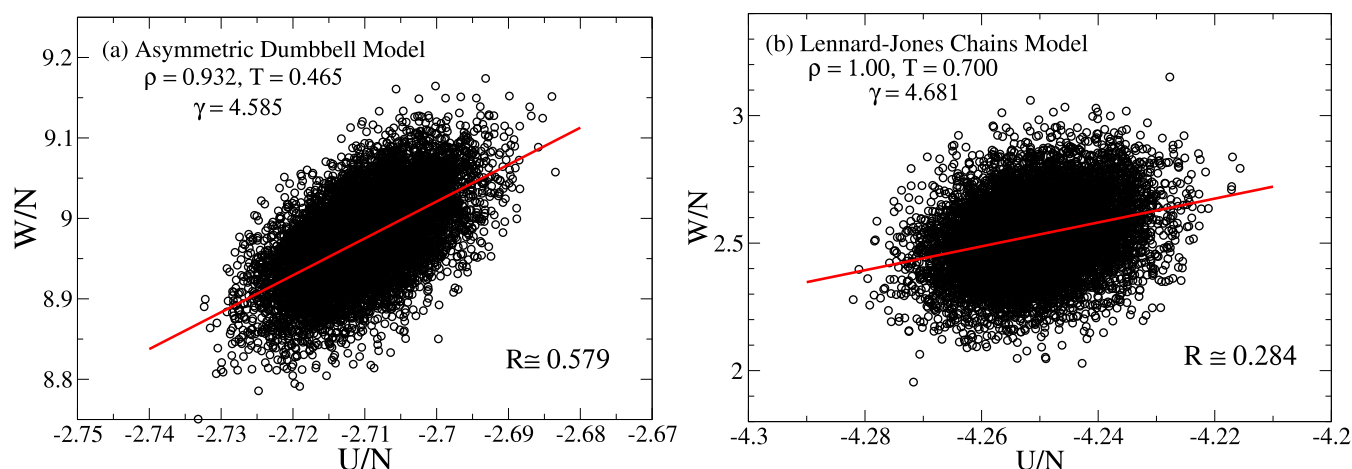


Figure 1. Scatter plots of equilibrium fluctuations of the virial and the potential energy. (a) Results for the asymmetric dumbbell model with harmonic bonds. (b) Results for the 10-bead flexible Lennard-Jones chain model with harmonic bonds. For both models the correlation coefficient R is much smaller than the criterion for an R -simple system, $R > 0.9$.¹

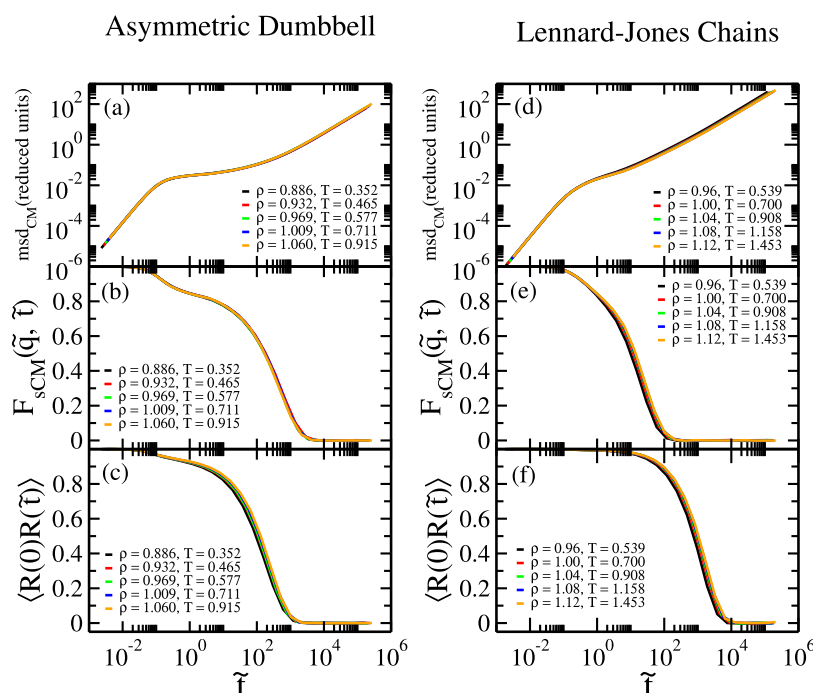


Figure 2. Invariance of the dynamics along state points determined by Olsen et al.²⁰ to define pseudoisomorphs. (a–c) Results for the asymmetric dumbbell model with harmonic bonds; (d–f) show results for the 10-bead Lennard-Jones chain model with harmonic bonds. (a, d) The reduced mean-square displacement of the center of mass as a function of reduced time. (b, e) The center-of-mass incoherent intermediate scattering function as a function of reduced time at the wave-vector corresponding to the first peak of the static structure factor. (c, f) The normalized end-to-end vector time-autocorrelation function, probing the decay of molecular orientation.

the change of dynamics induced by a pressure increase may be counteracted by increasing the temperature. Many systems, however, do not have isomorphs in the original sense of the word as lines of constant excess entropy,¹ which raises the question: Can some systems still have lines of (approximately) invariant structure and dynamics? This question motivates the below presented investigation of two molecular models.

Because S_{ex} is the part of entropy that refers to particle positions, isomorphs are configurational adiabats. These can be traced out in the thermodynamic phase diagram by using the generally valid statistical-mechanical relation¹

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

Evaluating the right-hand side by equilibrium NVT simulations, an isomorph is traced out by solving the differential equation eq 2 numerically using, e.g., the Euler or Runge–Kutta methods.¹¹

Isomorphs have been identified and validated for both atomic^{1,11–15} and molecular systems,^{10,16} and isomorph-theory predictions have been verified in experiments on glass-forming van der Waals molecular liquids.^{17,18} In molecular systems, isomorphs are found when bonds are modeled as con-

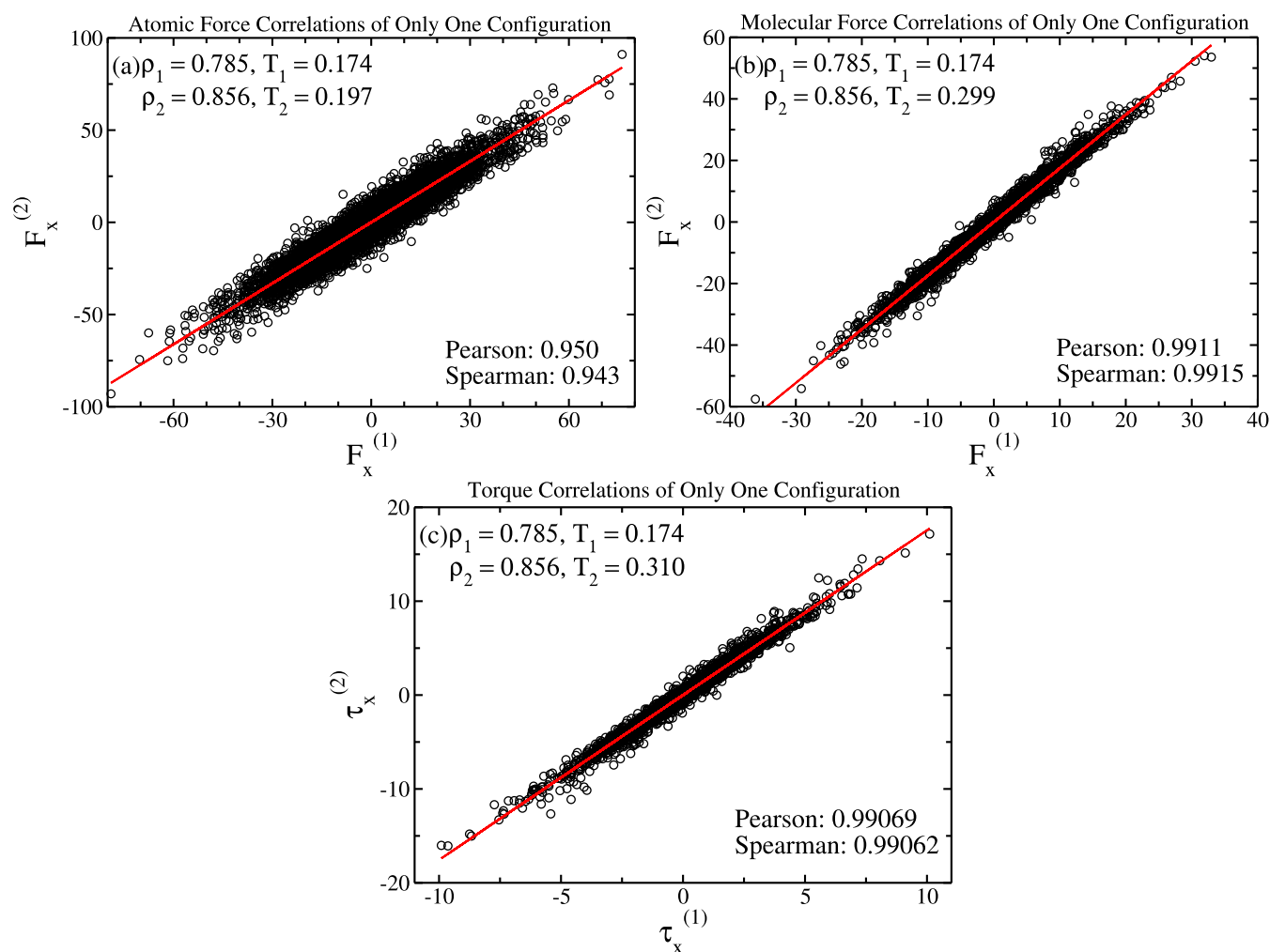


Figure 3. Force and torque correlations of a single configuration of the harmonic ASD model using center-of-mass scaling. Each point represents scaled and unscaled forces/torques. (a) Atomic-force method. The figure shows the x -coordinates of the reduced particle forces plotted against the same quantities of the uniformly scaled configuration. The temperature $T_2 = 0.197$ is identified by means of eq 3 (b) Molecular-force method. The figure shows the center-of-mass “molecular” forces before and after scaling, which have no contributions from the springs. In this case $T_2 = 0.299$. (c) Torque method. The figure shows the correlation between the torques before and after scaling ($T_2 = 0.310$).

straints,^{10,16} but not when the bonds are flexible.^{9,19,20} As an example, Figure 1 shows scatter plots of virial versus potential energy for the asymmetric dumbbell (ASD) and 10-bead Lennard-Jones chain (LJC) models, both with harmonic springs as commonly used in simulations.^{9,21} Neither model is R -simple; the virial potential-energy correlation coefficients are 0.579 and 0.284, respectively. As expected, these models do not have isomorphs (data not shown), i.e., structure and dynamics are not invariant along the curves of constant S_{ex} . Nevertheless, it has been found that both models have curves in the phase diagram of invariant structure and dynamics; these are termed “pseudoisomorphs”.^{9,16}

Since pseudoisomorphs are not configurational adiabats, eq 2 cannot be used to identify pseudoisomorphs in the phase diagram. In 2016 Olsen et al. presented a method for tracing out pseudoisomorphs involving the following steps:²⁰ (1) An equilibrium configuration is quenched to the nearest local minimum in the high-dimensional potential energy landscape, the so-called inherent state;²² (2) the Hessian matrix is diagonalized to find the vibrational spectrum of the inherent state; (3) the high-frequency part of the spectrum (related to the springs) is identified; (4) the scaling properties upon a

density change of the remaining part of the spectrum is used to identify the pseudoisomorph. This method works well but is very computationally demanding. Olsen et al. demonstrated that the method traces out pseudoisomorphs for the ASD and the flexible LJC models, demonstrating good though not perfect invariance of the dynamics probed via the incoherent intermediate scattering function. For comparison with later results, Figure 2 shows the dynamics probed via the mean-square displacement, incoherent intermediate scattering function, and orientational time-autocorrelation function, for the state points identified in ref 20.

The present paper proposes simpler methods for generating pseudoisomorphs based on the scaling properties of the forces of a single configuration.²³ This idea has been shown to work well not only for atomic systems like the Kob–Andersen binary Lennard-Jones mixture, but also for molecular models like the ASD model and the Lewis–Wahnstrom OTP model with rigid bonds.^{10,23–25}

II. METHODS

II.I. Models and Simulation Details. The ASD model is a toy model of toluene.^{10,26–33} We simulated a system of 5000

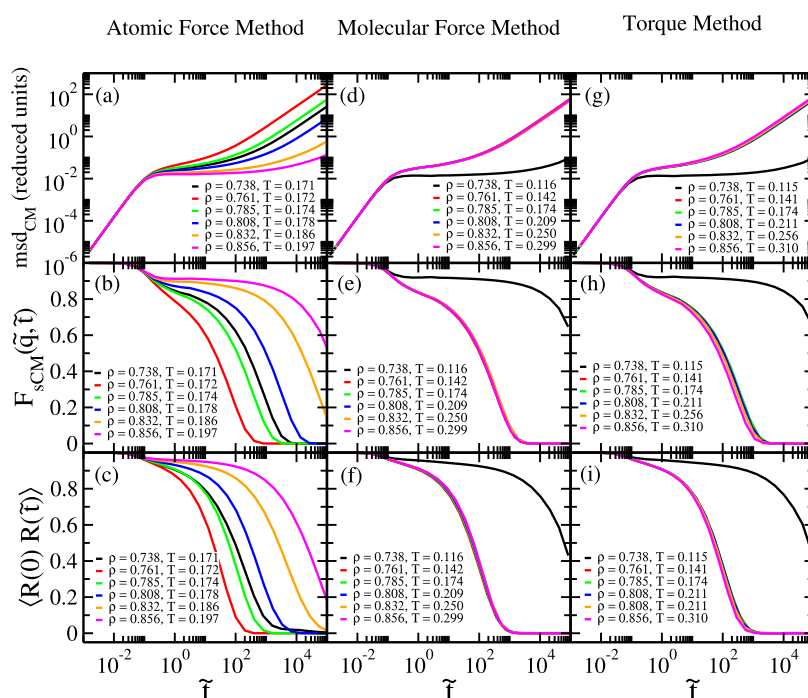


Figure 4. Testing for invariance of the reduced dynamics of the harmonic-spring ASD model using the three methods generating pseudoisomorphs by scaling a single configuration of the reference state point $(\rho_1, T_1) = (0.785, 0.174)$. Each method investigates the reduced center-of-mass mean-square displacement (upper figures), center-of-mass incoherent intermediate scattering function at the wave vectors corresponding to the first peak of the static structure factor (middle figures), and directional time-autocorrelation function probed via the autocorrelation function of the normalized bond vectors (bottom figures). (a–c) Results of the atomic-force method requiring invariant reduced forces between all atoms, i.e., including the harmonic bond contributions into eq 3. (d–f) Results of the molecular-force method requiring invariant reduced center-of-mass forces between the molecules. (g–i) Results of the torque method requiring invariant reduced torques on the molecules (eq 4).

ASD molecules defined as two different-sized spheres, a large (A) and a small (B) one.^{26,34,35} The spheres interact via Lennard-Jones (LJ) potentials, and in the units defined by the large sphere ($\sigma_{AA} \equiv 1$, $\epsilon_{AA} \equiv 1$, and $m_A \equiv 1$) the remaining LJ-parameters are $\sigma_{AB} = 0.894$, $\sigma_{BB} = 0.788$, $\epsilon_{AB} = 0.342$, $\epsilon_{BB} = 0.117$, $m_B = 0.195$. Bonds are modeled as harmonic springs with equilibrium length 0.584 and spring constant $k = 3000$.

The LJC model is a generic coarse-grained polymer model.^{36–39} We simulated 1000 10-bead LJC molecules. Nonbonded particles interact via a standard LJ potential, cutting and shifting the forces at 2.5σ . All particles are of same type and the potential parameters are set to unity: $\sigma = 1$, $\epsilon = 1$. Bonds are modeled as harmonic springs with equilibrium length 1 and spring constant $k = 3000$.

All Molecular Dynamics simulations were performed in the NVT ensemble with a Nose–Hoover thermostat and periodic boundary conditions, using RUMD that is an open-source molecular dynamics package optimized for GPU computing⁴⁰ (<http://rumd.org>).

II.II. Identifying Pseudoisomorphs via Force-Based Methods. Single-configuration force-based methods for generating isomorphs were introduced recently.^{23,25} The idea is the following. Given a configuration with particle coordinates \mathbf{R}_1 at the state point (ρ_1, T_1) , a uniform scaling to density ρ_2 is performed leading to $\mathbf{R}_2 = (\rho_1/\rho_2)^{1/3}\mathbf{R}_1$. For molecules, two variants of scaling can be applied: “center-of-mass scaling” where the molecular center-of-masses are scaled while all orientations and internal degrees of freedom are kept fixed, or “atomic scaling” where a uniform scaling is applied to all atoms, thus modifying also the intramolecular bond lengths. After scaling a configuration, the forces associated with the two

configurations, $\mathbf{F}(\mathbf{R}_1)$ and $\mathbf{F}(\mathbf{R}_2)$, are compared (\mathbf{F} is the vector of all forces). The temperature T_2 at the density ρ_2 is identified from the condition of invariant reduced forces. Specifically, $|\tilde{\mathbf{F}}(\mathbf{R}_1)| = |\tilde{\mathbf{F}}(\mathbf{R}_2)|$ implies²³

$$T_2 = \frac{|\mathbf{F}(\mathbf{R}_2)|}{|\mathbf{F}(\mathbf{R}_1)|} \left(\frac{\rho_1}{\rho_2} \right)^{1/3} T_1 \quad (3)$$

If the two force vectors are parallel, this leads to the forces being identical in reduced units, $\tilde{\mathbf{F}}(\mathbf{R}_1) = \tilde{\mathbf{F}}(\mathbf{R}_2)$. Assuming this is representative of all relevant configurations, it follows that structure and dynamics are invariant in reduced units because the same reduced-unit equation of motion applies at the two state points.^{6,41} We do not expect the force vectors before and scaling to be perfectly parallel, however, but eq 3 can still be used. Reference 23 proposed that for force-based method to work well, both the Pearson and Spearman correlation coefficients of the force components should be larger than 0.95 (the latter is defined as the Pearson correlation coefficient of the rank of the data).

Different variants of the method are arrived at by different interpretations of what exactly $\mathbf{F}(\mathbf{R})$ represents, e.g., the forces on all the atoms or just on the center-of-mass forces. We consider below also a variant based on invariance of torques in reduced units, $\tilde{\boldsymbol{\tau}}_1 = \tilde{\boldsymbol{\tau}}_2$, which leads to

$$T_2 = \frac{|\boldsymbol{\tau}_2|}{|\boldsymbol{\tau}_1|} T_1 \quad (4)$$

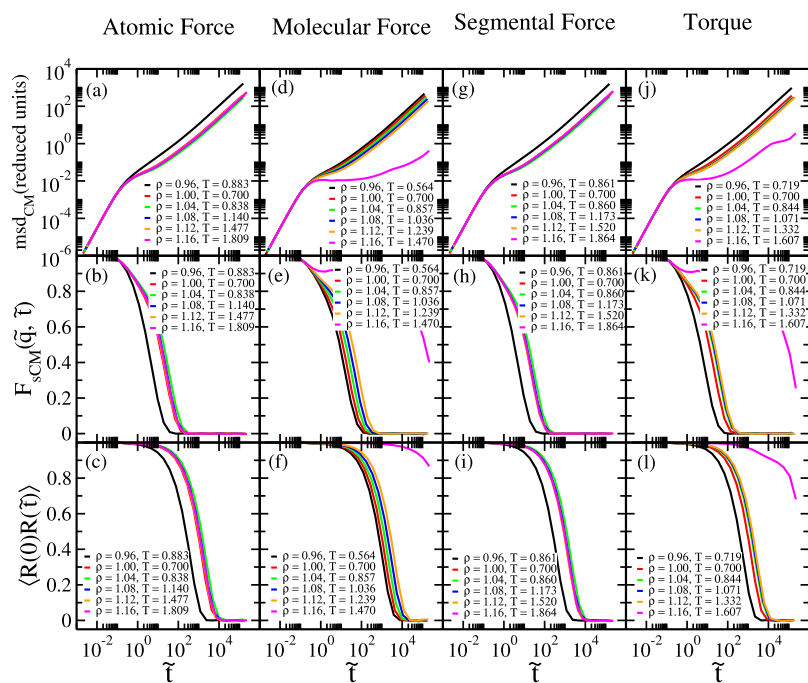


Figure 5. Dynamics of the harmonic-spring LJC model along proposed pseudoisomorphs. The reference state point is $(\rho_1, T_1) = (1.00, 0.700)$ and the density increase is 17%. The atomic-force and molecular-force methods both generate good pseudoisomorphs when increasing density compared to the reference state point. For both methods, decreasing the density leads to a higher temperature and a too fast dynamics. We currently have no explanation as to why this happens. Neither the molecular-force method nor the torque method result in good pseudoisomorphs. As density is increased, the predicted temperatures for both methods get smaller and smaller compared to those predicted by the atomic- and segmental-methods, leading to slower dynamics. At the highest density (magenta curves) the dynamics is much slower, which might indicate a glass-transition and/or (partial) crystallization. Since neither method works well, we have not investigated this further.

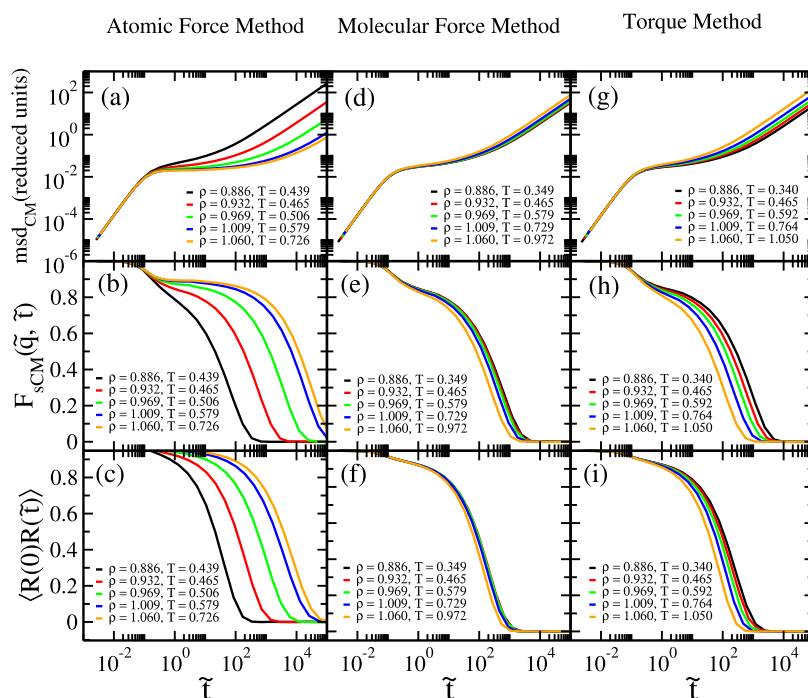


Figure 6. Dynamics of the ASD model along proposed pseudoisomorphs. The densities are here higher than in Figure 4. The density increase is 19%. For all three methods center-of-mass scaling was employed. The reference state point $(\rho_1, T_1) = (0.932, 0.465)$ is taken from ref 20. The molecular-force methods works best, but the invariance is not as good as at lower densities (Figure 4).

III. RESULTS

III.I. ASD Model. The three methods are applied to the ASD model in Figure 3, using center-of-mass scaling, i.e., $\mathbf{R}_{2,\text{cm}}$

$= (\rho_1/\rho_2)^{1/3}\mathbf{R}_{1,\text{cm}}$. The state point $(\rho_1, T_1) = (0.785, 0.174)$ is used as reference and $\rho_2 = 0.856$, i.e., a 9% density increase is considered. Figure 3(a) shows a scatter plot of the atomic-force components before and after scaling for a single

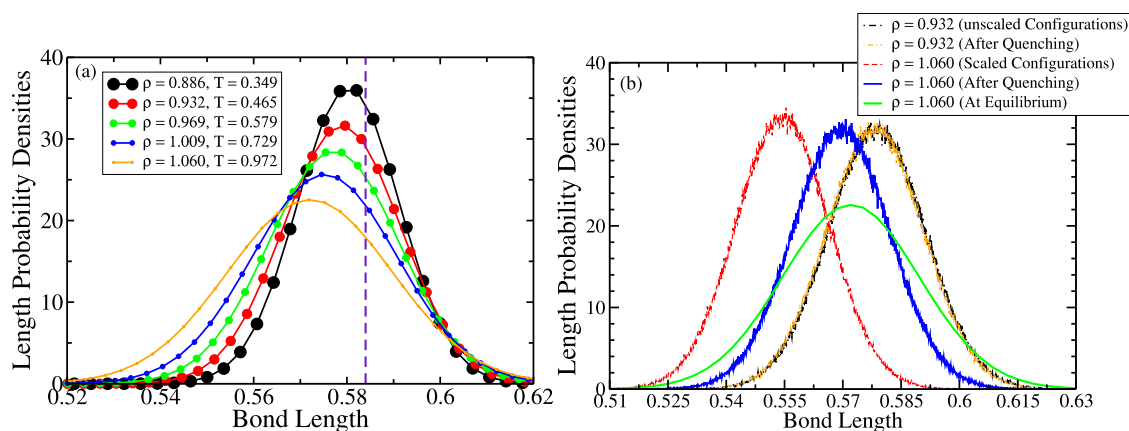


Figure 7. (a) Equilibrium distribution of ASD bond lengths at state points identified by the molecular-force method (see Figure 6(d–f)). Bonds are compressed when density is increased. This means that when a configuration is center-of-mass scaled from the reference state point to a (say) higher density, the resulting configuration is not representative of the equilibrium configurations at this density. (b) Quenching the system according to the constraint conditions (fixed center-of-mass and orientational direction of all molecules). Black: bond length distribution of original unscaled configuration at the reference state point. Orange: applying the quenching procedure to the unscaled configuration leads to virtually the same distribution. Red: atomic scaling to the new higher density leads to bond lengths that are considerably smaller than the ones in equilibrium at the new state point (green curve). Blue: center-of-mass scaling to the new higher density followed by the quenching procedure leads to a bond length distribution that is close to that of equilibrium at the new state point (green curve). Note: the procedure adds the same length “ l ” to all bonds, which leads to shift in the distribution leaving the shape invariant.

configuration; here $T_2 = 0.197$ is found by applying atomic forces in eq 3. Figure 3(b) shows a similar plot based on the “molecular” forces, i.e., the center-of-mass forces defined as the sum of all forces on the atoms of a given molecule. In this case the quite different temperature $T_2 = 0.299$ is arrived at and a significantly better correlation is obtained. Finally, Figure 3(c) shows the torque correlations of molecules of unscaled and scaled configurations. The correlation is here not far from that of the molecular forces; using eq 4 gives $T_2 = 0.310$.

For each of the three methods, Figure 4 compares results for the (same) dynamics at the state points, which the different methods predict identical dynamics. While the methods in principle require only a single configuration, for carefully comparing the methods, T_2 -values were obtained by averaging over 195 independent configurations. We find that the molecular-force method gives almost invariant dynamics, except at the lowest density (black curve) where negative pressure and phase separation is observed. The torque method gives similar, though slightly inferior results, while the atomic force method does not work well.

III.II. LJC Model. Next we turn to the 10-bead harmonic-spring LJC model for which one can use not only the three above methods, but also a fourth one based on invariant reduced segmental forces. These are defined as

$$\mathbf{F}_{\text{Seg},j} \equiv \frac{1}{d_j} \mathbf{F}_j + \frac{1}{d_{j+1}} \mathbf{F}_{j+1} \quad (5)$$

in which $\mathbf{F}_{\text{Seg},j}$ is the total force on particle j , i.e., including also the nonbonded interaction contributions, and d_j and d_{j+1} are the number of bonds that particles j and $j + 1$ are involved in. Clearly

$$\mathbf{F}_{\text{Mol}} = \sum_{j=1}^9 \mathbf{F}_{\text{Seg},j} \quad (6)$$

The results are quite different from the ASD results. Thus, the dynamics are to a good approximation invariant for the atomic- and segmental-force methods (Figure 5(g–i)), except at the

lowest density from reference point $(\rho_1, T_1) = (1.00, 0.700)$ at which the virial becomes negative. On the other hand, neither the molecular force method (d–f) nor the torque method (j–l) result in good pseudoisomorphs.

III.III. Pseudoisomorphs in the ASD Model at Higher Densities. In Figure 4 we applied the three force-based single-configuration methods to the ASD model and found best invariance of the dynamics using the molecular-force and, to a slightly less degree, torque methods. Figure 6 shows the results of applying the three methods at higher densities. The invariance of the dynamics is not as good as at lower densities (Figure 4). The molecular-force method works best, but no method works as well as the method of ref 20., compare Figure 2.

Figure 7(a) shows the distributions of bond lengths for simulations at the state points generated by the molecular-force method. The bonds are compressed when the density is increased, an effect that is not seen at the lower densities of Figure 4. This means that when a configuration from the reference state point is scaled to a higher density, the scaled configuration is not representative of equilibrium configurations at the new state point because the bonds are too long, an issue that becomes more serious at higher densities.

To eliminate the effects of the harmonic bonds, we introduce the following procedure: For a given configuration, fix the center-of-mass and orientation of each molecule. For this “constrained” system, add a length l to all bond lengths and minimize the potential energy with respect to l . We refer to this procedure as “quenching”, but note that the minimization only involves a single variable, the length l added to all bonds. When applied to an unscaled configuration, the bond length distribution remains largely unchanged (black and orange curves in Figure 7(b)). Now, consider the scaling of the original configuration to higher density, with the aim to achieve a bond length distribution close to that of the equilibrium at the new state point (green curve). Using center-of-mass scaling of the molecules leaves the bond lengths unchanged (black curve), whereas atomic scaling lead to too

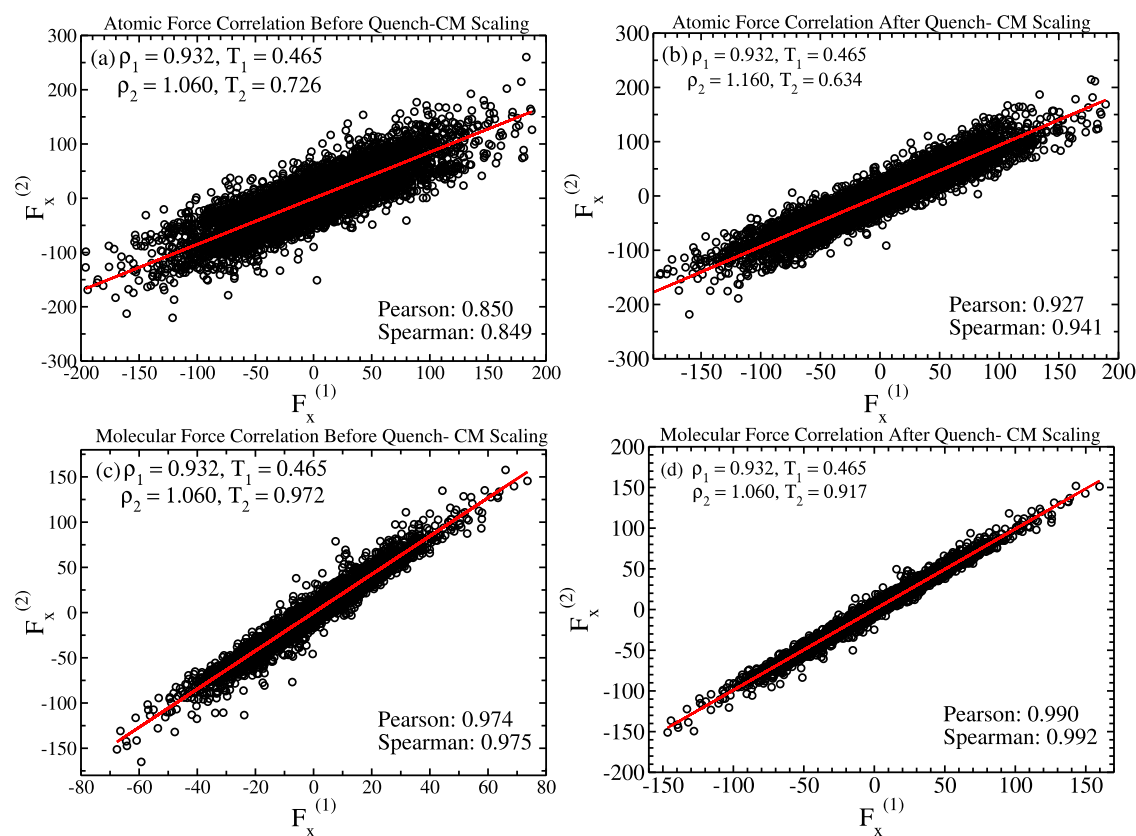


Figure 8. Correlation of atomic-force components, (a, b), and molecular-force components, (c, d), for the ASD model. A configuration is taken from a simulation at $(\rho_1, T_1) = (0.932, 0.465)$ and T_2 as previously calculated by means of eq 3. For both the atomic-force and molecular-force methods we find significantly better correlations between scaled and nonscaled forces components when applying a quench. Only the molecular forces fulfill the criterion that the Pearson and Spearman correlation coefficients are both above 0.95.²³

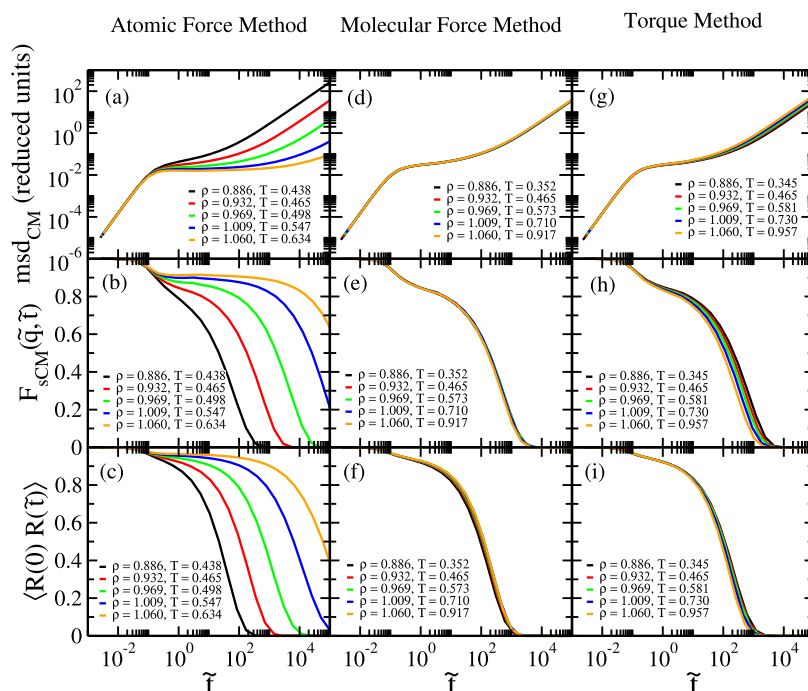


Figure 9. Testing the ASD model for invariance of the reduced dynamics using the three quench methods for generating pseudoisomorphs based on a single configuration from $(\rho_1, T_1) = (0.932, 0.465)$. In contrast to Figure 6, the scaled and nonscaled configurations were here quenched to a potential-energy minimum in order to eliminate the harmonic bond degrees of freedom; after this T_2 was determined as in Figure 6.

small bond lengths (red curve). Applying the quenching procedure after center-of-mass scaling shifts the distribution to shorter bond lengths (from the black line to the blue line), and the average bond length approaches that of the equilibrium distribution at the higher density (green line). This effectively eliminates the nonscaling degrees of freedom that likely cause the poor invariance observed in Figure 6.

Based on pairs of quenched configurations, one may again apply the atomic-force, molecular-force, and torque methods to generate state points with, hopefully, same dynamics. Specifically, we proceeded as follows. A single configuration is selected from an equilibrium simulation at the reference state point (density ρ_1). This configuration is scaled uniformly to the density of interest, ρ_2 . Both scaled and unscaled configurations were then quenched as described above in order to eliminate the bond vibrational degrees of freedom. After this the relevant forces/torques were evaluated and T_2 determined from eqs 3 and 4, respectively. Figure 8(a) shows the forces of a single scaled configuration versus those of the unscaled configuration before quenching, while (b) demonstrates better correlation after quenching; (c, d) show the correlations between the center-of-mass forces before and after quenching. The quench method leads to significantly better correlation, with correlation coefficient increasing from 0.850 to 0.934 in the atomic-force case and from 0.975 to 0.990 in the molecular (center-of-mass) force case.

The effect of quenching is tested in Figure 9, which is analogous to Figure 6 except that the temperatures T_2 are calculated based on quenched configurations. The best results are obtained with the molecular-force method, which was also the one that worked best in Figure 4. For this method we find excellent collapse of the reduced center-of-mass mean-square displacement as a function of time, as well as of the center-of-mass incoherent intermediate scattering function. The directional time-autocorrelation function shows a slightly worse collapse, but is nevertheless significantly better than without quenching. Comparing the results of the torque method with and without quenching shows that quenching also here significantly improves the invariance. Using atomic scaling gives the same results for the molecular force and torque methods after the system has been quenched (Table 1), while the atomic-force method gives results different from Figure 9.

Table 1. Predicted Temperature Using Atomic Scaling after Quenching (ASD Model)^a

density	$T (F_{\text{atomic}})$	$T (F_{\text{mol}})$	torque
0.886	0.444	0.352	0.345
0.932	0.465	0.465	0.465
0.969	0.494	0.573	0.581
1.009	0.540	0.710	0.730
1.060	0.624	0.917	0.957

^aNote that the molecular-force and torque methods give the same results as when center-of-mass scaling is used (Figure 9). $\rho = 0.932$ is the reference density in all cases.

IV. DISCUSSION

Genuine isomorphs do not exist in systems without strong virial potential-energy correlations, e.g., systems of molecules with harmonic bonds. For the ASD model and the flexible LJC model with harmonic bonds curves nevertheless exist along which the structure and dynamics are invariant to a good

approximation, so-called pseudoisomorphs.²⁰ These curves do not have invariant excess entropy, but otherwise they behave much like isomorphs by having approximately invariant structure and dynamics in reduced units. It would be interesting to investigate whether some coarse-grained description corresponds to an excess entropy that is invariant along the pseudoisomorphs in this paper, but we have not attempted this and instead prioritized to directly search for methods that identify pseudoisomorphs.

A previously discussed method for tracing out pseudoisomorphs in the thermodynamic phase diagram works well, but is quite complicated to apply in practice.²⁰ The present paper explored the possibility of tracing out pseudoisomorphs based on the simple requirement of invariant length of the reduced force vector of a single configuration after scaling. Although the focus above was on the dynamics, we note that for all three methods discussed the structure is also invariant to a good approximation, both with and without quenching (Figure 10).

Several closely related but different concepts have been introduced the last couple of decades in order to rationalize important findings of invariant structure and/or dynamics in the thermodynamic phase diagram. The present case of pseudoisomorphs for two realistic molecular models presents a good occasion for summarizing these concepts. One speaks about

- Excess-entropy scaling when the (reduced-unit) transport coefficients are invariant along the lines of constant excess entropy.^{42,43} Here DC signals the zero-frequency limit of, e.g., the diffusion coefficient or viscosity.
- Density scaling when invariant transport coefficients are observed along specific lines in the phase diagram, often described by $\rho^{\nu}/T = \text{Const.}$ ^{44,45}
- Isochronal superposition when entire linear-response relaxation functions are invariant along specific lines in the phase diagram.⁴⁶
- Isomorph invariance when structure and dynamics are invariant along the lines of constant excess entropy, termed isomorphs.^{1,6,41}
- Pseudoisomorphs when structure and dynamics are invariant along lines that are not of constant excess entropy.¹⁶
- Isodynes when dynamics, but not structure, is invariant along specific lines.^{47,48}

The most recent additions—pseudoisomorphs and isodynes—were introduced to describe liquids of more complex molecules, often with internal degrees of freedom. Our vision is that some modification of isomorph theory, e.g., arrived at via a suitable coarse-graining focusing on the most important degrees of freedom, may apply also here. At this point in time, however, it is clear that more work is needed in terms of gathering data for many different models to arrive at a coherent picture. Even the relation between pseudoisomorphs and isodynes is not clear. For instance, it is an open question whether large molecules with many internal degrees of freedom are pseudoisomorphs or just isodynes, e.g., without structural invariants. This will depend on the relevant coarse-graining; in fact, systems previously classified as having isodynes do have important parts of their structure factor being invariant along the same lines as the dynamics.^{47,48}

For the harmonic-bond ASD model the best method for tracing out pseudoisomorphs is the molecular-force method with center-of-mass scaling and quenching of the harmonic

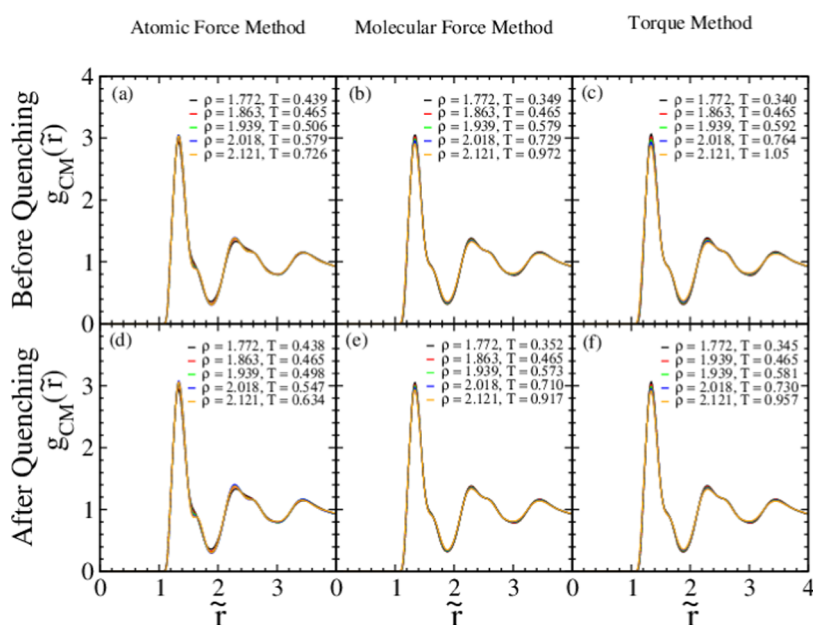


Figure 10. Testing the ASD model for invariance of the reduced-unit radial distribution function for the three different methods, without and with quenching, using $(\rho_1, T_1) = (0.932, 0.465)$ as reference state point. (a–c) Results for state points generated by the atomic-force, molecular-force, and torque methods; (d–f) show results for state points generated by the same methods after minimization. In all cases, structure is invariant to a good approximation.

bonds (Figure 9). At low densities, the quenching can be skipped (Figure 4). We conjecture that this method works on all small molecules with harmonic bonds, assuming of course that the systems in question have pseudoisomorphs. The fact that quenching improves the tracing out of pseudoisomorphs is significant by indicating that the internal degrees of freedom of medium sized molecular systems can largely be scaled out.

The molecular-force method does not work well for the 10-bead harmonic-bond LJ-chain model for which the best method is the atomic-force method with atomic scaling (Figure 5). That the atomic force method works best for long chains again is intuitively reasonable as a bead will not be aware that it is interacting with one from another chain or one on the same chain (apart from its nearest neighbors).

From a practical point of view one would like to have a single method that works for all molecular models with pseudoisomorphs, including the two models investigated here. The differences found can be interpreted as reflecting differences regarding which forces are important for the motion of the molecules. Despite the harmonic bonds, the ASD is relatively stiff and its motion is largely governed by the center-of-mass “molecular” force and the torque. If the scaling were perfect, both the molecular-force and the torque methods would lead to invariant dynamics. The fact that we find the molecular-force method to work better than the torque method can be interpreted as the molecular forces being more important than the torques for the motion of the molecules. It would be interesting to investigate whether molecular models exist for which the torque method works better than the molecular-force method. The molecular-force method does not work well for the LJC model. We interpret this as reflecting the fact that the center-of-mass motion does not determine the motion of this complex, flexible molecule, which should rather be thought of in terms of the motion of its beads.

V. CONCLUSIONS

Simple single-configuration force-based methods exist for tracing out pseudoisomorphs, which work as well as the complicated method of diagonalizing the Hessian before and after scaling.²⁰ No single-configuration method of general validity has been identified, however. More work is needed to investigate these and other methods; in this context we find it encouraging that the introduction of quenches after scaling improves all the methods studied.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the VILLUM Foundation’s Matter grant (VIL16515).

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