Self-averaging fluctuations in the chaoticity of simple fluids

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Bulk properties of equilibrium liquids are a manifestation of intermolecular forces. Here, we show how these forces imprint on dynamical fluctuations in the Lyapunov exponents for simple fluids with and without attractive forces. While the bulk of the spectrum is strongly self-averaging, the first Lyapunov exponent self-averages only weakly and at a rate that depends on the length scale of the intermolecular forces; short-range repulsive forces quantitatively dominate longer-range attractive forces, which act as a weak perturbation that slows the convergence to the thermodynamic limit. Regardless of intermolecular forces, the fluctuations in the Kolmogorov-Sinai entropy rate diverge, as one expects for an extensive quantity, and the spontaneous fluctuations of these dynamical observables obey fluctuation-dissipation-like relationships. Together, these results are a representation of the van der Waals picture of fluids and another lens through which we can view the liquid state.

Introduction. – Liquids live in a state between the structural order typical of solids and the dynamical randomness of gases [1, 2]. While molecular chaos underlies the existence of gaseous thermodynamic states, this notion, and Boltzmann’s Stosszahlansatz [3], are absent from the theories of liquids [4]. The coarse features of simple fluids are instead seen as a result of the forces between their molecular constituents [5]. Since van der Waals, the prevailing view has been that strong repulsive forces determine the structural arrangements of molecules in a liquid away from the critical point. Weak, longer-range attractive forces, though, have relatively little effect [6, 7]. This paradigm forms a basis for the statistical mechanics of equilibrium liquids [8–11] and, more recently, has been considered for the slow dynamics of supercooled liquids [12–14]. However, this view neglects the fluidity of liquid matter that comes from the incessant thermal motion of molecules, motion that, because of these intermolecular forces, is intrinsically chaotic [15]. It remains an open question how the liquid state emerges from the Lyapunov instability and deterministic chaos of molecular dynamics [16] and whether the van der Waals picture mirrors a dynamical perspective, where attractive and repulsive interactions play distinct roles in the emergent chaotic behavior of equilibrium liquids. In this Letter, we address this question.

A signature of the nonlinear dynamics of fluids, and any dynamical system exhibiting deterministic chaos, is the divergence of initially close phase space trajectories [17]. Finite-time Lyapunov exponents (FTLEs) are the exponential rates of divergence and important measures of the sensitivity to initial conditions characteristic of chaos. While their fluctuations on finite-time scales ultimately decay in the long-time limit [18, 19], it is unknown how these fluctuations scale in the thermodynamic limit for fluids. This fact is largely because FTLE calculations are limited to systems that are small or restricted to one or two spatial dimensions [20]. By overcoming this challenge, we show that the finite-size scaling of these fluctuations, that is, how they “self-average,” is a quantitative representation of the van der Waals picture.

Thermodynamic states are generally a consequence of the self-averaging of microscopic properties. A system self-averages its independent subsystems if a global observable is an average of that observable over the independent subsystems. More precisely, a system is self-averaging with respect to a property $X$ if the relative variance $R_X = \langle (X_N^2) - (X_N)^2 \rangle / (X_N)^2 \rightarrow 0$ as the system size $N \rightarrow \infty$, with averages over statistical samples, independent subsystems, noise, disorder, or independent time windows [21]. For equilibrium systems, the relative variance is $O(N^{-1})$ but more generally can be $R_X \simeq N^{-\gamma}$ with a wandering exponent $0 \leq \gamma \leq 1$.

Through finite-size scaling of Lyapunov exponent fluctuations and numerical estimates of $\gamma$, dissipative and Hamiltonian dynamical systems have begun to collect into universality classes. Previous work on dissipative, spatially extended dynamical systems in one and two dimensions has shown the self-averaging behavior of the largest Lyapunov exponent is not only dependent on the number of spatial dimensions but also distinct from the bulk of the Lyapunov spectrum. For these dissipative systems, the Lyapunov exponents are weakly self-averaging, $\gamma < 1$ [22, 23], with the dynamics of the first Lyapunov vector belonging to the Kardar-Parisi-Zhang (KPZ) universality class [24] and a $\gamma$ for the associated exponent that is related to the known critical exponents. The bulk exponents, however, belong to another, still unknown, universality class. There are one-dimensional Hamiltonian systems, such as the FPU-$\beta$ and $\Phi^4$ models, that stand in stark contrast. Fluctuations of the maximum Lyapunov exponent in these models are not self-averaging but instead diverge in the thermodynamic limit [19]. It is not yet clear whether this non-KPZ behavior [25, 26] is a sole consequence of long-range spatiotemporal correlations or a more universal feature of Hamiltonian dy-
nematics. By extending the finite-size scaling of the fluctuations of the Lyapunov spectrum to three-dimensional Hamiltonian systems, we show here the divergence is not universal, thus confirming the hypothesis of long-range correlations.

**Models of simple fluids and theory.**—We numerically simulate the dynamics of periodic Lennard-Jones (LJ) [27] and Weeks-Chandler-Andersen (WCA) [28] fluids in three spatial dimensions. The Hamiltonian of these \( N \)-particle systems is \( H(r_{ij}, p_k) = \sum_{k}^{2} p_{k}^2 / 2m + \sum_{i<j}^{N} V(r_{ij}) \). The interparticle interactions are specified by the pairwise potential \( V(r_{ij}) \) between the particles \( i \) and \( j \) a distance \( r_{ij} \) apart (inset of Fig. 1(a)). In the WCA fluid, particles interact through short-range repulsive forces and in the LJ fluid, particles also attract one another through comparatively longer-range forces. All quantities are in reduced units. (See Supplemental Material [SM] [29] Secs. I and II.)

Along with each constant energy trajectory of these equilibrium fluids, we simulate the corresponding tangent space dynamics, which limits the largest, computationally tractable system size to around 2000 particles, even leveraging recent computational advances [20]. Within the linearized limit, the expansion or the compression factor of the perturbation along the direction of the \( i \)th Lyapunov vector over time \( t \) is \( e^{\Gamma_i(t)} \). The associated FTLE is \( \lambda_i = \Gamma_i(t) / t \). For each trajectory, we calculate the finite-time Lyapunov spectrum, \( \{ \lambda_i \} \), and the finite-time Kolmogorov-Sinai (KS) entropy \( h_{KS} \) (i.e., the sum of the positive \( \{ \lambda_i \} \) using Pesin’s theorem [34]) from the set of Gram-Schmidt vectors [35, 36]. Algorithms for computing the covariant Lyapunov vectors do not readily scale to the system sizes we simulate here [37].

Our interest is in the self-averaging of fluctuations of the FTLEs and the finite-time KS entropy for simple fluids with and without attractive forces. We quantify fluctuations in the FTLEs over fixed time intervals, \( t \), with the diffusion coefficients \( \{ D(\lambda_i) \} \) [19, 22, 23] and the variance, \( \chi^2_{\lambda_i} \), of \( \{ \Gamma_i(t) \} \)

\[
tD(\lambda_i) = \chi^2_{\lambda_i} = \langle (\Gamma_i(t) - \lambda_i)^2 \rangle \, .
\]

Averages \( \langle \cdot \rangle \) are over an ensemble of \( 10^4 \) trajectories, each with \( t = 0.1 \) in reduced time units (SM [29] Sec. III). \( \langle \lambda_i \rangle \) is the long-time average of \( \lambda_i \). With these trajectory ensembles, we analyze the scaling of the diffusion coefficient for the entire Lyapunov spectrum, \( \{ D(\lambda_i) \} \), and the KS entropy rate, \( D(h_{KS}) \), with the number of particles, \( N \).

**Self-averaging of first Lyapunov exponent.**—An important measure of the degree of deterministic chaos in nonlinear dynamical systems is the Lyapunov exponent associated with the maximally expanding tangent space direction, \( \lambda_1 \). Over finite times, \( \lambda_1 \) concentrates around the long-time average with increasing system size, \( N \). Figure 1(a) shows representative empirical distributions of \( \lambda_1 \) for the WCA fluid over an ensemble of finite-time trajectories. We find similar results for the LJ fluid.

To quantify the decay rate of Lyapunov exponent fluctuations, we scale the number of molecules \( N \) and the volume \( V \) to ensure the thermodynamic limit of the microcanonical ensemble: \( N, V \to \infty \) keeping the number density \( \rho = N/V \) and energy density \( e = E/V \) fixed. At constant \( \rho \) and \( e \), the kinetic temperature is given by the equipartition theorem, \( T = 2 \langle E_{kin} \rangle / 3Nk_b \).

From scaling the system size of LJ and WCA fluids, we find that the diffusion coefficient \( D(\lambda_1) \) scales as a power law, \( O(N^{-\gamma}) \), with wandering exponent \( \gamma \) (Fig. 2). The magnitude of \( \gamma \) depends on the nature of the intermolecular forces and, in both cases, shows that fluctuations in \( \lambda_1 \) are weakly self-averaging, \( \gamma < 1 \). For the WCA liquid, where molecules are purely repulsive \( \gamma \approx 0.9 \). However, for the LJ liquid, where there are also attractions over

![FIG. 1.](image-url)  
(a) Empirical probability density functions of \( \lambda_1 \) from trajectory ensembles of Weeks-Chandler-Andersen fluids with varying numbers of particles \( N = 100, 200, 400 \) and \( 800 \) at the kinetic temperature \( T = 0.9 \) and number density \( \rho = 0.75 \). One inset is a semilog plot of the same data. The other inset shows the potential energy \( V(r_{ij}) \) for the interaction between Lennard-Jones and Weeks-Chandler-Andersen particles \( i \) and \( j \) as a function of the interparticle distance \( r_{ij} \). (b) Snapshot showing 5 out of the 16 system sizes we simulate with \( NVE \) molecular dynamics.

![FIG. 2.](image-url)  
Power law decay in the fluctuations of the finite-time Lyapunov exponent, \( \lambda_1 \), as measured by the diffusion coefficient, \( D(\lambda_1) \), with the number of particles, \( N \). Here, \( \lambda_1 \) is the exponent associated with the first Lyapunov vector. Data at three temperatures are shown for the (a) Lennard-Jones and (b) Weeks-Chandler-Andersen fluids. The points are simulation data and the lines are linear fits for systems with \( N \) from 100 to 2000 particles.
a few molecular diameters $\gamma \approx 0.85$. The difference between these $\gamma$ values is outside our statistical errors and shows that attractions act weakly to slow the decay of fluctuations.

Perturbative treatments of liquids in statistical mechanics build on the van der Waals picture. They assume the structure of a dense, monatomic fluid resembles that of a hard sphere fluid and, to a first approximation, the attractive interactions have little effect on the liquid structure [4]. Here, we see this picture through the fluctuations in $\lambda_1$, which decay at different rates for the LJ and WCA fluids. Repulsive forces dominate the decay of Lyapunov exponent fluctuations. Attractive forces not only slow the divergence of trajectories [15], they also diminish the rate $\gamma$ at which the thermodynamic states of liquids emerge through $\lambda_1$. These results are consistent with the idea that subvolumes of liquids made up of repulsive particles will become independent more quickly with increasing system size than those made of particles that can also attract over a relatively longer range. They also reinforce the intuition that the longer the range of intermolecular interactions, the slower the rate at which the largest Lyapunov exponent will self-average.

Although the weak self-averaging behavior of the largest Lyapunov exponent is sensitive to the length scale of the intermolecular forces, it is not dependent upon temperature. The wandering exponents for $\lambda_1$ of both fluids is independent of temperature in the range $0.7-1.1$ (SM [29] Sec. IV).

**Self-averaging of the bulk Lyapunov exponents.** The self-averaging of the largest Lyapunov exponent is distinct from the bulk of the spectrum (Fig. 3). And, for the fluids and conditions here, it measures the relative importance of attractions and repulsions in the emergent dynamics of simple liquids. Other observables, such as the kinetic and potential energy, however, do not. Instead, the kinetic and potential energy fluctuations are strongly self-averaging (SM [29] Sec. V) with $\gamma \approx 1$ independent of the intermolecular forces or temperature. Attractive forces also do not measurably affect the self-averaging behavior of the bulk Lyapunov exponents: all exponents in the spectrum beyond the first self-average strongly, $\gamma \approx 1$. Previous work also found that the scaling of the first Lyapunov exponent fluctuations with system size are markedly different from the bulk of the spectrum in both conservative and dissipative, one-dimensional dynamical systems [22, 23].

Both the WCA and LJ fluids under $NVE$ conditions have symmetric Lyapunov spectra [15] as a result of the conjugate pairing rule [38, 39] and the conservation of phase space volume by Liouville’s theorem. Figures 3(a) and 3(c) show this symmetry in the diffusion coefficients of the Lyapunov spectra, $\{D(\lambda_i)\}$, for the LJ and WCA liquids. As a function of the spectral index $i$, the diffusion coefficients are symmetric about half of the number of phase space dimensions, $i = 3N$ [22].

Figure 3 shows representative results for the finite-size scaling of the fluctuations in $\{\lambda_i\}$. The insets in (b) and (d) show the scaling of $D(\lambda_i/3N)$ with $N$ for the LJ and the WCA liquids, respectively, for several scaled indices, $i/3N$, at $T = 0.9$. Our simulations of 16 systems span 100 to 2000 particles ($N = 100, 200, \ldots, 1100, 1300, \ldots, 1900, 2000$). The number of positive Lyapunov exponents and the range of the index, $i$, grows as $3N$, so the scaled index, $i/3N$, is intensive. Given the symmetry of $D(\lambda_i)$, we focus on the positive exponents $\{\lambda_i\}$. We see that $\{D(\lambda_i/3N)\}$ scales as a power law, $N^{-\gamma}$ with $\gamma \approx 1$ for all exponents and both the LJ and the WCA fluids (SM [29] Sec. VI). Furthermore, we find the scaled diffusion coefficient $D(\lambda_i/3N)N^{-\gamma}$ data collapse onto a single curve as a function of the scaled index.

While we model the fluids as three-dimensional Hamiltonian systems, we do not detect the divergence of fluctuations of FTLEs in the thermodynamic limit seen in one-dimensional Hamiltonian lattices, the FPU-$\beta$ and $\Phi^4$ models [19]. The wandering exponent of the first Lyap-
The rate of self-averaging of Lyapunov exponent fluctuations depends on the number of spatial dimensions. Weak self-averaging of $\lambda_1$ for one- and two-dimensional systems with weak correlations is characterized by a $\gamma$ of $1/2$ and 0.839, respectively [22, 23]. The wandering exponents for the three-dimensional LJ and WCA systems are higher, 0.85 and 0.9. Because the KPZ critical exponents are known in lower dimensions, dynamical systems can be assigned to the KPZ universality class. But, this is not the case in three dimensions, so an assignment for the LJ and WCA fluids is not currently possible. Still, the agreement between the wandering exponents in fluids with and without attractive forces is evidence that the bulk of the Lyapunov vectors do belong to the same (albeit unknown) universality class, despite the longer range of the LJ interaction potential compared to WCA.

Strong self-averaging of the bulk Lyapunov exponents is so far unique to these simple fluids. In one-dimensional systems with short-range correlations, for example, the bulk Lyapunov spectrum self-averages weakly with $\gamma \approx 0.85$ [22, 23]. These lower dimensional systems also have an extensive and additive KS entropy, so this comparison also suggests that the strong self-averaging of the bulk exponents in simple fluids does not necessarily lead to these properties of the long-time KS entropy [15]. While it is well known from the van der Waals picture that repulsions dictate liquid structure, our results show that this picture is also apparent in the fluctuations of the Lyapunov exponents. Attractions have a measurable effect on only the most unstable Lyapunov direction.

**Self-averaging of the Kolmogorov-Sinai entropy rate and fluctuation-dissipation relations.** Another important quantity characterizing dynamical systems is the finite-time KS entropy: the sum of the positive FTLEs, $h_{KS}(t) = \sum_{i}^{+} \lambda_i(t)$. The fluctuations in the KS entropy, though important in fluctuation theorems, are less explored compared to those of the FTLEs. Again, we measure the finite-time KS entropy fluctuations with the diffusion coefficient. The scaling of $D(h_{KS})$ with system size is a power law $N^{\gamma}$ with $\gamma \approx 1$, as shown in Figs. 4(a) and (b), for both the LJ and the WCA fluids. The divergence of fluctuations in the KS entropy supports recent evidence of its system-size extensivity; the converging Lyapunov exponent fluctuations also confirm their system-size intensivity [15]. Because the KS entropy for these fluids is system-size extensive, fluctuations in the KS entropy density, $h_{KS}/N$, are self-averaging and decay as $N^{-1}$ to the thermodynamic limit.

As for the Lyapunov exponents, temperature does not affect the scaling (SM [29] Sec. IV). However, the magnitude of the diffusion coefficient is temperature dependent. To determine the temperature dependence, we ran additional simulations for the LJ and the WCA fluids between $T = 0.4$ and 2.0. From these simulations, for all the Lyapunov exponents, the first and the bulk, and the Kolmogorov-Sinai entropy for both Lennard-Jones and Weeks-Chandler-Andersen fluids, $D$ varies as $k_BT$ over the temperatures and numbers of particles we consider (SM [29] Sec. IV). Together with the self-averaging of these dynamical observables, the linear dependence of their diffusion coefficients on temperature suggest an empirical fluctuation-dissipation relation for chaoticity, $D \propto k_BT N^{\gamma}$, akin to the Einstein-Smoluchowski relation in real space, $D = \mu k_BT$. These results, however, connect the rate at which trajectories chaotically diffuse through phase space and the equilibrium temperature.

In summary, the dominance of repulsive forces over attractive forces in the dynamics of fluids is manifest in the fluctuations of the Lyapunov spectrum. We showed the first Lyapunov exponent self-averages, but only weakly, for three-dimensional Hamiltonian models of simple fluids. Weak attractions merely act to slow the rate of decay of fluctuations scaling to the thermodynamic limit. The convergence of the fluctuations associated with the first Lyapunov exponent for the three-dimensional Hamiltonian systems here is distinct from the divergent behavior of the one-dimensional Hamiltonian models studied to date. We attribute this difference to the short-range interparticle forces in the WCA and LJ fluids. These forces affect the wandering exponent of $\lambda_1$ but not the strongly
self-averaging nature of the bulk exponents. Consequently, the fluctuations in the KS entropy diverge as one expects for an extensive thermodynamic quantity.

From the wandering exponents, the bulk Lyapunov vectors of Lennard-Jones and Weeks-Chandler-Andersen fluids belong to the same, as yet unknown, universality class. What is clear is that the classes of the first Lyapunov vectors are distinct. It remains to be seen whether the spatial dimension, the length scale of interparticle interactions, or both influences the rate at which fluctuations decay in the bulk of the spectrum. Still, it is tempting to speculate that increasing the length scale of attractive forces would further slow the convergence and, eventually, even cause fluctuations to diverge. Regardless of intermolecular forces, for simple equilibrium liquids, we find evidence that the spontaneous fluctuations of these dynamical observables obey fluctuation-dissipation like relationships. Altogether, our results give an alternate view of the van der Waals picture of liquids, a view that opens up the possibility of examining emergent dynamical signatures at the liquid-gas critical point, in viscous liquids, or in self-organizing systems [40], where we anticipate long-range correlations to cause nontrivial self-averaging behavior.

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[1] J. A. Barker, D. Henderson, Rev. Mod. Phys. 48, 587 (1976).
[2] T. S. Ingebrigtsen, T. B. Schroder, J. C. Dyre, Phys. Rev. X 2, 011011 (2012).
[3] L. Boltzmann, Lectures on Gas Theory. (Dover Publishing Co., New York, 1995).
[4] J. P. Hansen, I. R. McDonald, Theory of Simple Liquids (Academic Press, London, England, 1986).
[5] B. Widom, Science 157, 375 (1967).
[6] J. D. van der Waals, On the Continuity of the Gaseous and Liquid States, (Dover, New York, 2004).
[7] J. D. Weeks, K. Katsov, K. Vollmayr, Phys. Rev. Lett. 81, 4400 (1998).
[8] S. Fisk, B. Widom, J. Chem. Phys. 50, 3219 (1969).
[9] J. A. Barker, D. Henderson, J. Chem. Phys. 47, 4714 (1967).
[10] J. A. Barker, D. Henderson, Annu. Rev. Phys. Chem. 23, 439 (1972).
[11] D. Chandler, J. D. Weeks, H. C. Andersen, Science 220, 787 (1983).
[12] L. Berthier, G. Tarjus, Phys. Rev. Lett. 103, 170601 (2009).
[13] U. R. Pedersen, T. B. Schroder, J. C. Dyre, Phys. Rev. Lett. 105, 157801 (2010).
[14] Z. E. Dell, K. S. Schweizer, Phys. Rev. Lett. 115, 205702 (2015).
[15] M. Das, A. B. Costa, J. R. Green, Phys. Rev. E 95, 022102 (2017).
[16] H. Bosetti, H. A. Posch, Commun. Theor. Phys. 62, 451 (2014).
[17] P. Gaspard, G. Nicolis, Phys. Rev. Lett. 65, 1693 (1990).
[18] A. Pikovsky, A. Politi, Lyapunov Exponents, (Cambridge University Press, Cambridge, England, 2016).
[19] D. Pazó, J. M. López, A. Politi, Phys. Rev. Lett. 117, 034101 (2016).
[20] A. B. Costa, J. R. Green, J. Comput. Phys. 246, 113 (2013).
[21] I. M. Lifshitz, S. A. Gredeskul, L. A. Pastur, Introduction to the Theory of Disordered Systems (Wiley, New York, 1988).
[22] P. V. Kuptsov, A. Politi, Phys. Rev. Lett. 107, 114101 (2011).
[23] D. Pazó, J. M. López, A. Politi, Phys. Rev. E 87, 062909 (2013).
[24] M. Kardar, G. Parisi, Y.-C. Zhang, Phys. Rev. Lett. 56, 889 (1986).
[25] A. Pikovsky, A. Politi, Phys. Rev. E 63, 036207 (2001).
[26] M. Romero-Bastida, D. Pazó, J. M. López, M. A. Rodriguez, Phys. Rev. E 82, 036205 (2010).
[27] J. E. Jones, Proc. R. Soc. A 106, 463 (1924).
[28] J. D. Weeks, D. Chandler, H. C. Andersen, J. Chem. Phys. 54, 5237 (1971).
[29] See Supplemental Material for the details of models, molecular dynamics simulations, calculation of $D(\lambda)$, temperature dependence of the diffusion coefficients, kinetic and potential energy fluctuations associated with NVE trajectories, statistical fluctuations of $\gamma$ for the bulk Lyapunov exponents and system-size scaling of $\langle D(\lambda) \rangle$. This material includes Refs. [30–33].
[30] D. J. Wales, R. S. Berry, J. Phys. B: At. Mol. Opt. Phys. 24, L351-L357 (1991).
[31] S. D. Stoddard, J. Ford, Phys. Rev. A 8, 1504 (1973).
[32] J. R. Green, J. Jellinek, R. S. Berry, Phys. Rev. E 80, 066205 (2009).
[33] R. J. Hinde, R. S. Berry, D. J. Wales, J. Chem. Phys. 96, 1376 (1992).
[34] Y. B. Pesin, Russ. Math. Surveys 32, 55 (1977).
[35] H. Fujisaka, Prog. Theor. Phys. 70, 1264 (1983).
[36] G. Benettin, L. Galgani, A. Giorgilli, J.-M. Strelcyn, Meccanica 15, 9 (1980).
[37] F. Ginelli, P. Poggi, A. Turchi, H. Chaté, R. Livi, A. Politi, Phys. Rev. Lett. 99, 130601 (2007).
[38] S. Sarman, D. J. Evans, G. P. Morriss, Phys. Rev. A 45, 2233 (1992).
[39] Ch. Dellago, H. A. Posch, Phys. Rev. Lett. 78, 211 (1997).
[40] J. R. Green, A. B. Costa, B. A. Grzybowski, I. Szleifer, Proc. Natl. Acad. Sci. U.S.A. 110, 16339 (2013).