Entropy Scaling Laws in Self Propelled Glass Formers

Sachin C.N. and Ashwin Joy

Department of Physics, Indian Institute of Technology Madras, Chennai - 600036, India
(Dated: December 4, 2019)

Predicting transport from equilibrium structure is a challenging problem in liquid state physics. Here we probe a glass forming liquid composed of self-propelled “active” particles and show that increasing the duration of self-propulsion \( \tau_p \) makes the pair excess entropy \( S_2 \) more negative, thereby reducing the number of accessible configurations per particle. At moderate values of effective temperature \( T \), the self-diffusivity is Arrhenius and in a reduced form obeys a Dzugutov like scaling law \( D^* \sim e^{\frac{g}{T}} \), directly yielding us the scaling formula \( S_2 \sim -1/T \). In the strongly super-cooled regime, Dzugutov law does not apply and the entropy follows a power law \( S_2 \sim -1/T^\beta \) all the way up to the glass transition \( T_g \). To demonstrate generality, we set the particle interactions to be purely repulsive (PR) in one case and Lennard-Jones (LJ) in the other, and find that in both the cases, the reported scaling laws are robust over three decades of variation in \( \tau_p \). Our results may apply to transport in active colloidal suspensions, passive tracers in bacterial baths, and self-propelled granular media, to mention a few.

Liquids in which the constituent particles are self-propelled or “active” can display a class of collective behavior that is typically not observed in conventional systems \[1\]-[4]. The coherent motion of these active particles has been shown to act as a precursor to flocking-an exotic ordered phase that arises when the mean velocity \( \langle \vec{v} \rangle \neq 0 \), with examples ranging from bird flocks and insect swarms to granular matter and dense colloids \[3\]-[9]. Other notable mentions where self-propulsion can profoundly affect liquid dynamics are jamming \[10\], phase separation \[11\]-[12] and phase transitions \[13\]-[14]. It is therefore natural to ask how activity modulates the dynamics and structure of a liquid especially at low temperatures where collective behavior is dominant. An important problem that has recently witnessed a sharp surge of interest is to establish the role of self-propulsion in the dynamics of super-cooled liquids nearing the glass transition \[15\]. Preliminary works in this area remain inconclusive on whether self-propulsion mitigates \[10\] or enhances \[17\] sluggish dynamics near a glass transition. The role of “activity” in modifying the potential energy landscape may help in understanding these contradicting claims \[13\]. The presence of an equilibrium counterpart or lack thereof in the sluggish dynamics of these self-propelled liquids therefore presents as an important research direction. Our letter focuses on this direction and reports a detailed investigation of the structure and transport in a model active glass forming liquid. In what follows, we will provide robust scaling laws for pair excess entropy - a quantity that is directly amenable in particle resolved experiments \[19\]. We use the following numerical model of a “living” fluid where the governing equation for the \( i^{th} \) particle, reads as:-

\[
\dot{\vec{r}}_i = \frac{1}{m \gamma} \left( -\nabla_i U + \vec{f}_i \right) \\
\dot{\vec{f}}_i = \frac{1}{\tau_p} \left( -\vec{f}_i + \sqrt{2m \gamma k_B T} \, \eta_i \right)
\]  

Put simply, the particle dynamics is governed by an overdamped Ornstein-Uhlenbeck type of stochastic process that has been used extensively to model athermal active fluids \[20\]-[23]. In this model, self-propulsion is described completely using only two parameters, namely, the effective temperature \( T \) and a certain time scale \( \tau_p \), the former manifesting in the strength of the self-propulsion force \( \vec{f}_i \), and the latter indicates the duration of \( \vec{f}_i \). We take \( \eta_i \) to be a Gaussian white noise with zero mean and unit variance. The parameter \( \gamma \) refers to the friction coefficient and \( U \) denotes the potential energy due to particle interactions. In this letter, we have used this model for self propulsion in a well known glass former and will report scaling laws for pair excess entropy and self diffusivity in the super-cooled regime. It should be noted that the Eq. 1 reduces to the standard overdamped Brownian dynamics as \( \tau_p \to 0 \) and has been shown to satisfy detailed balance in the small \( \tau_p \) limit \[25\]. The friction coefficient \( \gamma \) is set to unity in all the runs and Eq. 1 is integrated using a fully implicit scheme and a time step of \( 10^{-5} \) \[26\]. In the following we provide the details of our numerical work.

We have used the Kob-Andersen binary glass forming liquid with 80% large (\( L \)) and 20% small (\( S \)) particles interacting via the Lennard-Jones (LJ) potential energy \[27\]

\[
U_{LJ} = \sum_{i < j} 4 \epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right].
\]

To demonstrate generality, we repeated simulations on a purely repulsive (PR) potential energy \[28\]

\[
U_{PR} = \sum_{i < j} 1.945 \epsilon_{ij} \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{15.48}
\]

and observed qualitatively similar results. For both types of interactions, we took \( \epsilon_{LL}, \sigma_{LL} \) and \( \sqrt{m \sigma_{LL}^2/\epsilon_{LL}} \) as the units of energy, length and time respectively. In these units, the potential parameters become \( \epsilon_{SS} = \)
0.50, $c_{LS} = 1.50$, $\sigma_{SS} = 0.88$, and $\sigma_{LS} = 0.80$. In order to derive our scaling laws, we need to first set up the connection between the dynamics and the underlying structure in our model active liquid. To that end, we have made extensive measurements on pair excess entropy $S_2$ (explained below) that essentially captures the correction to the ideal gas entropy due to pair correlations. It is then straightforward to compute $S_2$ using the prescription by Wallace [29] -

$$S_2 = -2\pi \sum_{\mu} \chi_{\mu} \sum_{\nu} \rho_{\nu} \int [1 + g_{\mu\nu}(r)\{\ln g_{\mu\nu}(r) - 1\}] r^2 dr$$

(4)

We are now in position to connect structure with liquid diffusivity, and for this we use the prescription of Hoyt et al [33] to obtain a normalized total diffusivity in terms of the scaled contributions coming from $S$ and $L$ type particles-

$$D^* = \left[ \frac{D_L}{\Gamma_L} \right]^{\chi_L} \left[ \frac{D_S}{\Gamma_S} \right]^{\chi_S}$$

(5)

where $D_{\mu}$ is the partial diffusivity of $\mu$ type particles, calculated from mean squared displacement. The scale factors are given by

$$\Gamma_{\mu} = 4 \sqrt{\frac{\pi k_B T}{m}} \sum_{\nu} \sigma_{\mu\nu} g_{\mu\nu}(\sigma_{\mu\nu}) \rho_{\nu}$$

(6)

with $\mu, \nu = \{S, L\}$, as before and $\rho_L = 0.96$, $\rho_S = 0.24$. In Figure 2, we show a plot of $D^*$ vs. $S_2$ at various values of self propulsion. It is evident from the figure that Dzugutov like scaling law [30]

$$D^* = D_0 \exp(\alpha S_2),$$

(7)

applies in the moderate range of super-cooling at all values of $\tau_p$, the parameters $D_0$ and $\alpha$ being dependent on $\tau_p$. It should be noted that the scaling law (Eq.7) does not work at deep super-cooling, possibly due to the breakdown of ergodicity at these temperatures [34]. It is important to stress here that at moderate super-cooling, the entropy scaling law works for over three decades of variation in $\tau_p$ and therefore allows us to build robust scaling laws for $S_2$ in this regime. To connect $S_2$ with $T$, we turn our attention to the temperature dependence of diffusivity $D^*$. Figure 3 shows a plot of $D^*$ vs. $T$ at various values of $\tau_p$ used in our work. Data collapse at high temperature ($T > 1.0$) is evidently achieved by using the Arrhenius form of diffusivity [35],

$$D^* = D_A e^{-E_A/RT} \ (\text{High } T).$$

(8)
On the other hand, in the low temperature regime (inset: Figure 3), we observe an excellent data collapse using the Vogel-Fulcher (VF) form
\[
D^* = D_{VF} e^{-E_{VF}/(T - T_g)} \quad \text{(Low } T),
\]
We now present a way to extract reliable scaling laws for pair excess entropy \(S_2\) that is directly from particle positions in a typical experiment. In the high temperature regime, we eliminate \(D^*\) between equations (9) and (10) to get a scaling
\[
S_2 = (-1/\alpha) \ln (D_0/D_{Ar}) - E_{Ar}/\alpha T \quad \text{(High } T).
\]
A similar relation was qualitatively suggested in [36] in the context of equilibrium passive liquids and we find it remarkable this scaling law holds for a wide range of our non-equilibrium active liquid. The role of persistence time \(\tau_p\) is therefore limited to modulating the intercept, \((1/\alpha)\ln (D_0/D_{Ar})\) and the slope, \(E_{Ar}/\alpha\) of the entropy relation. At low temperatures however, we observe that the entropy follows a power law
\[
S_2 = S_2^0 (T_g/T)^\beta \quad \text{(Low } T),
\]
all the way up to the lowest temperature where we can achieve an effective equilibrium. The fitting parameters \(T_g\) and \(S_2^0\) respectively, the glass transition temperature and the pair excess entropy at \(T_g\). Note \(S_2^0 < 0\) is required to make \(S_2 < 0\). Finally, to demonstrate the generality of our scaling laws, we plot \(S_2\) vs. \(T\) in figure 1 for both Lennard-Jones (LJ) and purely repulsive (PR) particle interactions using filled and empty symbols respectively. In both the figures, the solid lines demonstrate the high temperature scaling law \(S_2 \sim -1/T\) (from Eq. (10)) with the slope and intercept represented by \(-E_{Ar}/\alpha\) and \((-1/\alpha)\ln (D_0/D_{Ar})\), respectively. We can explain this on grounds that the liquid structure manifests in the number of accessible states available per atom and therefore strongly affects the rate of cage diffusion. Since cage breaking is necessary for the onset of diffusive regime, it is natural to expect that reduction in \(D\) is concomitant with increasing \(-S_2\). At lower temperatures however, the liquid becomes increasingly non-ergodic and the Arrhenius behaviour is lost, directly pressing the need for an alternative scaling law. Our data at low temperatures is in excellent agreement with a power law scaling \(S_2 \sim -1/T^\beta\) that remains valid up to the lowest effective temperature accessible to us. A numerical fit of our data to this power law scaling directly reveals the numerical glass transition temperature \(T_g\). To test the generality of our predictions, we have also verified our scaling laws with data obtained from a liquid with purely repulsive particle interactions at various val-
ues of persistence time [Ref. Fig. 4]. We therefore assert that these scaling laws are universal in nature and should be of great utility to soft matter physicists interested in active glass forming liquids.

Summary: Our paper reports a careful study of pair excess entropy $S_2$ and its connection to diffusivity $D$, thus proving the existence of Dzugutov like scaling law in a model active glass forming liquid. To our knowledge, such studies have been performed only in the domain of equilibrium liquids and no account exists in literature that deliberates on the nature of this connection in non-equilibrium “living” liquids. We focus on a model “living” liquid that is essentially far from equilibrium and where the notion of a effective temperature can be established only in the steady state. The role of self propulsion in mitigating transport is carefully examined and is seen to be a precursor for sluggish dynamics. By systematically examining transport and structure, we are able to predict scaling laws for the pair excess entropy that are both independent of the type of particle interactions, and also valid over a wide range of persistence time. As our findings are universal in nature, we believe that they could be of great interest to an experimentalist exploring the transport phenomena in “living” fluids, especially when particle positions are resolved at the microscopic level, and $S_2$ becomes directly amenable.

We thank Ethayaraja Mani and Abhijit Sen for discussions and comments on the manuscript. All simulations were done on the VIRGO super cluster of IIT Madras.

_____________________________

[1] L. Berthier, Phys. Rev. Lett. 112, 220602 (2014)
[2] D. Gonzalez-Rodriguez, K. Guevorkian, S. Douezan, and F. Brochard-Wyart, Science 338, 910 (2012).
[3] I. Theurkauff, C. Cottin-Bizonne, J. Palacci, C. Ybert, and L. Bocquet, Phys. Rev. Lett. 108, 268303 (2012).
[4] A. Sokolov and I. S. Aranson, Phys. Rev. Lett. 109, 248109 (2012).
[5] J. Toner and Y. Tu, Phys. Rev. E 58, 4828 (1998).
[6] J. Toner, Y. Tu, and S. Ramaswamy, Annals of Physics 318, 170 (2005).
[7] M. C. Marchetti, J.-F. Joanny, S. Ramaswamy, T. B. Liverpool, J. Prost, M. Rao, and R. A. Simha, Reviews of Modern Physics 85, 1143 (2013).
[8] A. Cavagna and I. Giardina, Annu. Rev. Condens. Matter Phys. 5, 183 (2014).
[9] A. Kaiser, A. Snezhko, and I. S. Aranson, 3 (2017), 10.1126/sciadv.1601469
[10] C. Bechinger, R. Di Leonardo, H. Löwen, C. Reichhardt, G. Volpe, and G. Volpe, Reviews of Modern Physics 88, 045006 (2016).
[11] G. S. Redner, M. F. Hagan, and A. Baskaran, Phys. Rev. Lett. 110, 055701 (2013).
[12] Y. Fily, S. Henkes, and M. C. Marchetti, Soft matter 10, 2132 (2014).
[13] A. Czirók, A.-L. Barabási, and T. Vicsek, Physical Review Letters 82, 209 (1999).
[14] Y. Fily and M. C. Marchetti, Physical review letters 108, 235702 (2012).
[15] J. R. Gomez-Solano, A. Blokhuis, and C. Bechinger, Phys. Rev. Lett. 116, 138301 (2016).
[16] R. Mandal, P. J. Bhuyan, M. Rao, and C. Dasgupta, Soft Matter 12, 6268 (2016).
[17] E. Flenner, G. Szamel, and L. Berthier, Soft matter 12, 7136 (2016).
[18] R. Ni, M. A. C. Stuart, and M. Dijkstra, Nature communications 4, 2704 (2013).
[19] I. Yokoyama and S. Tsuchiya, Materials Transactions 43, 67 (2002).
[20] T. F. F. Farage, P. Krinninger, and J. M. Brader, Phys. Rev. E 91, 042310 (2015).
[21] N. Koumakis, C. Maggi, and R. Di Leonardo, Soft matter 10, 5695 (2014).
[22] G. Szamel, E. Flenner, and L. Berthier, Phys. Rev. E 91, 062304 (2015).
[23] U. M. B. Marconi and C. Maggi, Soft matter 11, 8768 (2015).
[24] F. Ginot, I. Theurkauff, D. Levis, C. Ybert, L. Bocquet, L. Berthier, and C. Cottin-Bizonne, Phys. Rev. X 5, 011004 (2015).
[25] E. Fodor, C. Nardini, M. E. Cates, J. Tailleur, P. Visco, and F. van Wijland, Phys. Rev. Lett. 117, 038103 (2016).
[26] R. Mannella and V. Palleschi, Phys. Rev. A 40, 3381 (1989).
[27] W. Kob and H. C. Andersen, Phys. Rev. E 51, 4626 (1995).
[28] U. R. Pedersen, T. B. Schroder, and J. C. Dyre, Physical review letters 105, 157801 (2010).
[29] D. C. Wallace, The Journal of Chemical Physics 87, 2282 (1987), https://doi.org/10.1063/1.453158.
[30] M. Dzugutov, Nature 381, 137 (1996).
[31] A. Baranyai and D. J. Evans, Physical Review A 40, 3817 (1989).
[32] A. Joy, Physics of Plasmas 24, 010702 (2017).
[33] J. Hoyt, M. Asta, and B. Sadigh, Physical Review Letters 85, 594 (2000).
[34] M. Dzugutov, Journal of Physics: Condensed Matter 11, A253 (1999).
[35] T. Wang, F. Zhang, L. Yang, X. Fang, S. Zhou, M. J. Kramer, C.-Z. Wang, K.-M. Ho, and R. E. Napolitano, Scientific reports 5, 10956 (2015).
[36] G. X. Li, C. S. Liu, and Z. G. Zhu, Phys. Rev. B 71, 094209 (2005)