

## Diffusivity anomaly in modified Stillinger-Weber liquids

Shiladitya Sengupta,<sup>1</sup> Vishwas V. Vasisht,<sup>2</sup> and Srikanth Sastry<sup>1,2</sup>

<sup>1</sup>TIFR Centre for Interdisciplinary Sciences, 21 Brundavan Colony, Narsingi, Hyderabad 500089, India

<sup>2</sup>Theoretical Sciences Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur Campus, Bangalore 560064, India

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By modifying the tetrahedrality (the strength of the three body interactions) in the well-known Stillinger-Weber model for silicon, we study the diffusivity of a series of model liquids as a function of tetrahedrality and temperature at fixed pressure. Previous work has shown that at constant temperature, the diffusivity exhibits a maximum as a function of tetrahedrality, which we refer to as the diffusivity anomaly, in analogy with the well-known anomaly in water upon variation of pressure at constant temperature. We explore to what extent the structural and thermodynamic changes accompanying changes in the interaction potential can help rationalize the diffusivity anomaly, by employing the Rosenfeld relation between diffusivity and the excess entropy (over the ideal gas reference value), and the pair correlation entropy, which provides an approximation to the excess entropy in terms of the pair correlation function. We find that in the modified Stillinger-Weber liquids, the Rosenfeld relation works well above the melting temperatures but exhibits deviations below, with the deviations becoming smaller for smaller tetrahedrality. Further we find that both the excess entropy and the pair correlation entropy at constant temperature go through maxima as a function of the tetrahedrality, thus demonstrating the close relationship between structural, thermodynamic, and dynamical anomalies in the modified Stillinger-Weber liquids. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4862146>]

### I. INTRODUCTION

Many theoretical approaches aim to relate the dynamical behaviour of liquids to their structural and thermodynamic properties. Semi-empirical relations like the Rosenfeld,<sup>1,2</sup> the Dzugutov,<sup>3</sup> and the Adam-Gibbs<sup>4</sup> relations offer a few examples. In the absence of a completely satisfactory microscopic theory, such relations serve as guiding principles with which to rationalize dynamics in the liquid state for different substances and conditions, even while the domain of their applicability continues to be subject to scrutiny. Particularly stringent tests of the applicability of such relations are offered by cases where dynamical properties of liquids (such as water and silicon) show anomalous behaviour as functions of control parameters like temperature and pressure. One such anomaly, relevant to our present study, is the diffusivity anomaly in water, manifested in the presence of a maximum in the diffusivity as a function of pressure.

In this paper we study the well-known Stillinger-Weber (SW) model for silicon and vary the strength ( $\lambda$ ) of the three body interaction in this potential, in addition to the temperature ( $T$ ) at fixed pressure ( $P = 0$ ), to obtain the liquid state properties in a  $\lambda - T$  phase diagram. It has been shown earlier that by tuning  $\lambda$  the model can be turned into a good glass-former,<sup>5</sup> for a range of  $\lambda$  values marked by the competition between cubic diamond and BCC crystal structures for the most stable state at low temperatures. Further, the diffusivity at constant temperature and pressure shows a non-monotonic dependence on  $\lambda$ ,<sup>5</sup> displaying a maximum at intermediate values of  $\lambda$  where the system is a good glass-former. It is tempting to seek the explanation of this diffusivity anomaly in the struc-

tural and thermodynamic changes leading to good glass forming behaviour, which we explore, through an analysis of the relationship between diffusivity, and entropy, *via* the Rosenfeld scaling relationship (which we describe below). While understanding anomalous diffusivity behaviour offers insights into the properties of a system, it also helps to critically examine to what extent dynamics can be related to structure and thermodynamics *via* Rosenfeld-like scaling relations and consequently how strongly the anomaly in diffusivity reflects the presence of structural and thermodynamic anomalies in this model.

Previous studies have indicated that structural, thermodynamic, and dynamic anomalies have interesting interrelations. In the case of water, Errington and Debenedetti observed<sup>6</sup> that the region of the phase diagram which shows anomalous behaviour in density is enclosed by the region of diffusivity anomaly which in turn is surrounded by a region of structural anomaly. Such nesting of anomalies implies that the origin of dynamic and thermodynamic anomalies may be attributed to that of structural anomalies. However, the question of whether such behaviour is universal or specific to water is still open.<sup>7,8</sup> Anomalies in diffusivity have also been explained in terms of anomalies in the configurational entropy *via* the Adam-Gibbs relation, e.g., in water (anomaly as a function of density)<sup>9,10</sup> and in generalized Lennard-Jones potentials (anomaly as a function of temperature).<sup>11</sup>

In this paper we study the anomaly in diffusivity as a function of the strength of the 3-body interaction in the Stillinger-Weber potential<sup>12,13</sup> for silicon. The SW potential is written as a sum of a two-body, isotropic interaction

$u_2(r_{ij})$  and a three-body, anisotropic interaction  $u_3(r_{ij}, r_{jk}, r_{ik})$  which favours locally tetrahedral geometry:  $U_{SW} = \sum_{pairs} u_2 + \lambda \sum_{triplets} u_3$ . Here  $\lambda$  represents the strength of the anisotropic interaction. In the original SW model,  $\lambda = 21$ . While the original SW model is a poor glass-former, it was shown by Molinero *et al.*<sup>5</sup> that as  $\lambda$  gradually decreases, there is a domain  $\lambda = 17.5$ – $20.25$  where the model turns into a good glass-former. Molinero *et al.*<sup>5</sup> showed that, at zero pressure, as  $\lambda$  is decreased, the diffusivity along the melting line undergoes a minimum in the glass-forming region, around  $\lambda = 18.75$ . On the contrary, Molinero *et al.*<sup>5</sup> pointed out that the diffusivity at constant temperature as a function of  $\lambda$  at zero pressure, undergoes a maximum in the range  $\lambda = 17.5$ – $18$ , i.e., in the glass-forming domain. This behaviour of *isothermal*, *isobaric* diffusivity as a function of  $\lambda$  is the focus of the present study.

The (dimensionless) diffusivity ( $D^*$ ) can be related to the excess entropy ( $S_E$ ) (the total entropy *minus* the ideal gas entropy at the same density) *via* the Rosenfeld scaling relation:  $D^* = D\rho^{1/3}(k_B T/m)^{-1/2} \approx A \exp(bS_E)$ , where  $\rho$ ,  $T$ , and  $m$  are the density, temperature, and particle mass, respectively, and  $A$ ,  $b$  are the constants. Often, the excess entropy is substituted by the pair correlation entropy ( $S_2$ ) (defined below), which is easier to compute. In the context of the present work,  $S_2$  also offers a way of assessing to what extent the changes in structure (as accounted for by pair correlations) account for the total change in entropy. In this work, we thus compute both the excess entropy ( $S_E$ ) and the pair-correlation entropy ( $S_2$ ) and analyze them as a function of the 3-body potential strength. If the Rosenfeld scaling relation between diffusivity and entropy ( $S_E$ ,  $S_2$ ) is obeyed in the modified SW model (for a general  $\lambda$ ), then the excess and the pair correlation entropy at constant pressure and temperature should also go through maxima in the same  $\lambda$  range and provide a rationalization of the observed maximum of isothermal diffusivity.

The organization of the paper is as follows: In Sec. II we describe the simulation details. In Sec. III we discuss the Rosenfeld scaling relation and define the relevant quantities. In Sec. IV we show the main results. Finally in Sec. V we summarize the study and present the main conclusions.

## II. SIMULATION DETAILS

The interaction potential of the modified Stillinger-Weber model<sup>5,12</sup> is of the form

$$U_{SW} = \sum_{i<j} u_2(r_{ij}) + \lambda \sum_{i<j<k} u_3(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k), \quad (1)$$

where  $u_2$  is the two-body term and  $u_3$  is the three-body term, and  $\lambda$  represents the strength of the three-body interaction. The form of the potentials  $u_2$  and  $u_3$  and the units of mass, energy, and length are defined in Ref. 12. All the potential parameters are kept the same as in Ref. 12 except  $\lambda$  which is varied in the range  $\lambda=16$ – $21.5$ . At each  $\lambda$ , constant pressure and temperature (NPT) molecular dynamics (MD) simulations were done at zero pressure ( $P = 0$ ) over a range of temperatures for  $N = 512$  particles in a cubic box with periodic boundary conditions using details as in Ref. 14 but

employing an efficient algorithm for the energy and force calculations<sup>15,16</sup> as well as using the LAMMPS package.<sup>17</sup> All results are reported in *reduced units*, with respect to the SW model parameters (e.g., densities are reported in units of  $\sigma^{-3}$  where  $\sigma = 0.20951$  nm).

In the reduced units, with units of energy = 209.5 kJ/mol and of mass =  $28.0855 \times 10^{-3}$  kg/mol, respectively, the integration time step is  $dt = 0.005$ . The Runlength at each state point is at least  $60 \times 10^6$  MD steps.

## III. DEFINITIONS

### A. The Rosenfeld scaling relation

Rosenfeld proposed,<sup>1,2</sup> based on studies in purely repulsive inverse power law and Lennard-Jones potentials, that the diffusivity ( $D$ ) expressed in a dimensionless form ( $D^*$ ) can be related by a simple empirical formula to the excess entropy  $s_E \equiv S_E/Nk_B$ :

$$D^* = D\rho^{1/3}(k_B T/m)^{-1/2} \approx A \exp(bs_E), \quad (2)$$

where  $A$  and  $b$  are constants that can have different values for different systems.<sup>1,2</sup>

### B. Diffusivity

The diffusivity is measured from the long time limit of the mean squared displacements ( $\langle r^2 \rangle$ ) using the Einstein relation:

$$\lim_{t \rightarrow \infty} \langle r^2 \rangle = 6Dt.$$

### C. The excess entropy

The excess entropy at a given temperature and pressure is the entropy of the liquid in excess over the entropy of an ideal gas at the same temperature and pressure:

$$S_E = S_{liquid} - S_{ideal}. \quad (3)$$

In the present study, the excess entropy is computed by performing thermodynamic integration of derivatives of appropriate free energies. First, excess entropy is calculated for the original SW model ( $\lambda = 21$ ). At zero pressure, a high temperature ( $T_{ref} = 0.33$ ) above the liquid-gas critical point is chosen as the reference ideal gas state with zero excess entropy. The integration path consists of the following segments: (a) along the isotherm at  $T_{ref}$ , from zero density to a density  $\rho_{up} = 0.4775$  chosen from the  $P = 0$  isobar; (b) then along the isochore at  $\rho_{up}$  from  $T_{ref}$  to a temperature  $T_h = 0.095$  such that  $P(\rho_{up}, T_h) = 0$ ; (c) then along the zero pressure isobar from  $T_h$  to the target temperature  $T$ . Next, using the excess entropy at  $\lambda = 21$  to be the reference, excess entropies for modified Stillinger-Weber liquids (arbitrary  $\lambda$ ) are calculated by integrating the derivative of Gibbs free energy  $G$  with respect to  $\lambda$  at a constant temperature and zero pressure. Since the interaction potential is of the form  $U = U_2 + \lambda U_3$ , the derivative  $\frac{\partial G}{\partial \lambda}$  is the (ensemble averaged) three body part  $U_3$  of the interaction.

## D. The pair-correlation entropy

The pair-correlation entropy is defined as

$$\frac{S_2}{Nk_B} = -2\pi\rho \int_0^\infty [g(r) \ln g(r) - g(r) + 1]r^2 dr. \quad (4)$$

One can quite generally expand the excess entropy in terms of contributions from  $n$  - *particle* correlation functions as<sup>18-21</sup>

$$S_E = S_2 + S_3 + \dots, \quad (5)$$

where  $S_2$  is the pair correlation entropy,  $S_3$  is the three-particle entropy coming from three-particle correlation function  $g^3(r)$ , etc. Consequently,  $S_E$  is often approximated by the first term in the expansion, i.e.,  $S_2$  which is computationally cheaper as it depends only on the pair correlation function  $g(r)$ .

## IV. RESULTS

The range of state points studied, all of which are at zero pressure, is shown in Fig. 1 in the  $\rho - T$  and  $T - \lambda$  planes. In the upper panel of Fig. 1, we show the well-known density anomaly of the original SW model ( $\lambda = 21$ ) with the maximum occurring at  $T = 0.057$ . The density maximum for

$\lambda = 21$  along  $P = 0$  isobar have earlier been located to be at  $T = 0.055$ .<sup>22</sup> In the modified SW liquids (arbitrary  $\lambda$ ), the work of Hujo *et al.*<sup>23</sup> has shown that the density anomaly occurs in the range  $20 \leq \lambda \leq 26.4$  and vanishes at both lower and higher values of  $\lambda$ . In Fig. 1 we show that as the strength  $\lambda$  of the anisotropic part of the SW potential decreases, the temperature of maximum density gradually decreases and finally the density anomaly disappears for  $\lambda < 19.5$ —at least in the range of temperatures explored here. Thus the modified SW model can be turned from an anomalous liquid into a normal liquid by tuning  $\lambda$ . The lower panel of Fig. 1 shows the  $T - \lambda$  phase diagram. The vertical lines with symbols show the state points studied here. The circles and the squares indicate melting points, respectively, to BCC and cubic diamond crystals, reported in Ref. 5. The locus of melting temperatures forms a V-shaped curve where the minimum melting point occurs at  $\lambda = 18.75$  which is a triple point for coexistence of liquid, diamond cubic, and BCC phases.<sup>5</sup> Around the triple point, the range  $17.5 \leq \lambda \leq 20.25$  was identified in Ref. 5 to be a good glass-forming range.

Having described the range of the control parameters explored in the present study, we next discuss the analysis of the Rosenfeld scaling relation between diffusivity and excess

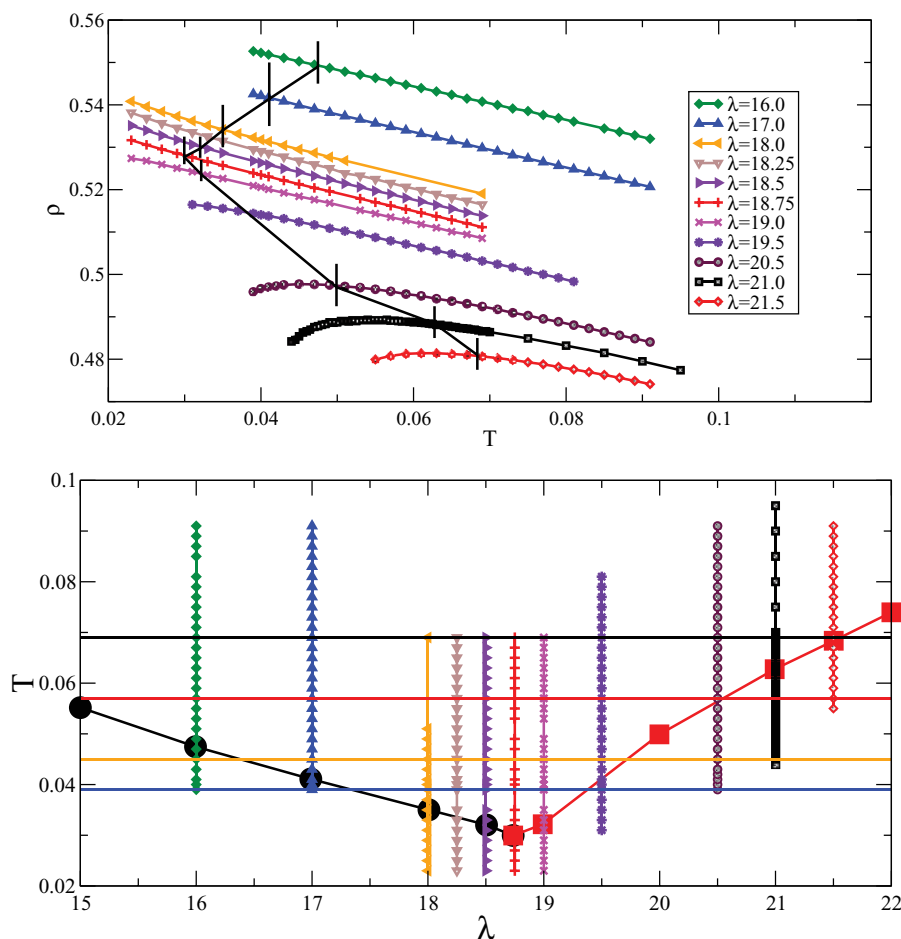


FIG. 1. Upper panel:  $\rho$  vs.  $T$  phase diagram for the mSW model showing the range of the state points explored in the present study. The lines connecting the data are guide to eyes. The vertical lines are the melting temperatures reported in Ref. 5 joined by a line representing the locus of the melting temperatures at different  $\lambda$ 's, demarcating the high  $T$  and the supercooled liquids. Lower panel:  $T$  vs.  $\lambda$  phase diagram for the mSW model showing the range of the state points explored in the present study. The circles and the squares represent the melting temperatures reported in Ref. 5. The horizontal lines indicate the representative temperatures chosen to calculate isothermal diffusivities.

entropy in the modified Stillinger-Weber liquids in Fig. 2. We find that above melting temperatures (indicated by vertical lines), the modified Stillinger-Weber liquids indeed obey the Rosenfeld relation but there are systematic deviations below melting temperatures. We have verified that a rescaling of the entropy and diffusivities does not produce data collapse at low temperatures. Thus, in addition to the deviations from Rosenfeld scaling, the behaviour at low  $T$  does not conform to any other universal form. However, we see that as  $\lambda$  decreases, the extent of deviation from the Rosenfeld relation below melting temperatures also gradually decreases. Since the Rosenfeld relation was originally proposed for liquids above melting temperatures, it is not surprising that there is a systematic deviation in the supercooled regimes. Rosenfeld himself noticed that the relationship between excess entropy and transport coefficients is not exponential everywhere on the phase diagram, even in simple liquids, e.g., for dilute gases the form is a power law.<sup>2</sup> For dense fluids, previous studies<sup>24–28</sup> have found that the exponential form holds at moderate to high temperatures but breaks down upon supercooling ( $s_{ex} < -4$  for simple liquids). However, in simple liquids it is generally found<sup>25–28</sup> that while the functional form changes, the relation between excess entropy and transport coefficients continues to show a universal behaviour.

Earlier studies have found<sup>1,2,29</sup> that for isotropic potentials (e.g., hard sphere, Lennard-Jones, inverse 12th power law, and one-component plasma), the coefficients  $A$  and  $b$  in the Rosenfeld relation are approximately independent of the interaction potentials. In the present study, the anisotropy of the interaction can be tuned by tuning  $\lambda$ , hence the quasi-universality of the Rosenfeld relation can be tested. In the inset of Fig. 2, we show that in the range  $16 \leq \lambda \leq 21.5$ , the coefficients  $A$  and  $b$  vary considerably, although for  $\lambda > 18.5$  and  $\lambda < 18.5$ , the variation considerably reduces, and  $A$  and  $b$  may be considered quasi-universal in these two regimes. Fur-

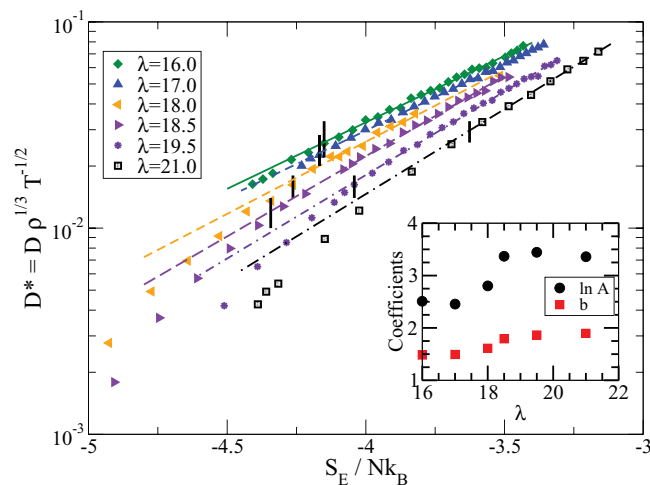


FIG. 2. Comparison of the *dimensionless* isobaric diffusivity  $D^* = \frac{\rho^{1/3}}{(k_B T/m)^{1/2}} D$  vs. the per particle excess entropy  $s_E = S_E/Nk_B$  for the modified SW model at different  $\lambda$ 's. Vertical bars denote melting temperatures. At each  $\lambda$ , data above the melting temperature are fitted to the Rosenfeld relation:  $D^* = A \exp(bs_E)$ . The Rosenfeld scaling relation is obeyed above the melting point ( $T_m$ ), but systematic deviations are observed in the supercooled state, the deviations being stronger for larger  $\lambda$ . *Inset*:  $\lambda$  dependence of the coefficients  $A$  and  $b$  in the Rosenfeld relation.

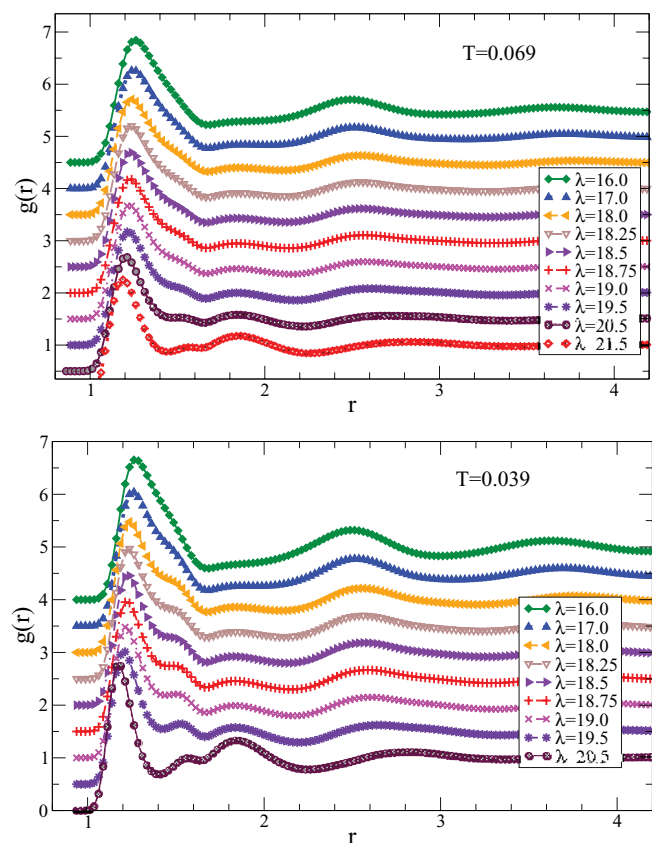


FIG. 3. The  $\lambda$  dependence of the pair correlation function  $g(r)$  at two representative temperatures.

ther, we note that in another model liquid with isotropic interactions, namely, the Kob-Andersen model<sup>30</sup> the values of  $A$  and  $b$  are lower<sup>26</sup> than the values obtained in the present work. This is consistent with the trend observed in the present study that the coefficients  $A$  and  $b$  decrease as the strength of the anisotropic interaction  $\lambda$  decreases.

Next we test to what extent the pair correlation entropy  $S_2$  can be used to approximate the excess entropy  $S_E$  in the modified SW liquids. Pair correlation entropies  $S_2$  are computed from the pair correlation functions  $g(r)$  which are shown for different  $\lambda$ 's in Fig. 3, at two representative temperatures. We see that as  $\lambda$  decreases, the first peak of  $g(r)$  gradually shifts to higher  $r$ . We also note that the shoulder between the first and the second peak of  $g(r)$ , more prominent at the low temperature, gradually disappears as  $\lambda$  decreases. In Fig. 4 we compare  $S_2$  to  $S_E$  for different  $\lambda$  and show that indeed for the original SW model ( $\lambda = 21$ ),  $S_2$  is approximately proportional to  $S_E$  although as the inset of Fig. 4 shows,  $S_2$  is clearly not an overwhelmingly dominant term in the expansion (5). The inset also shows that in the modified SW liquids (arbitrary  $\lambda$ ), the relative contribution of  $S_2$  to  $S_E$  gradually increases as the strength  $\lambda$  of the anisotropic interaction decreases which is expected, since higher order correlation entropies may play a greater role in determining the total entropy for the more anisotropic interactions.<sup>31,32</sup> However, Fig. 4 also shows that the degree to which there is a nearly constant proportionality between  $S_2$  and  $S_E$  also reduces as  $\lambda$  decreases, which is surprising, and needs to be further investigated. Fig. 5 shows

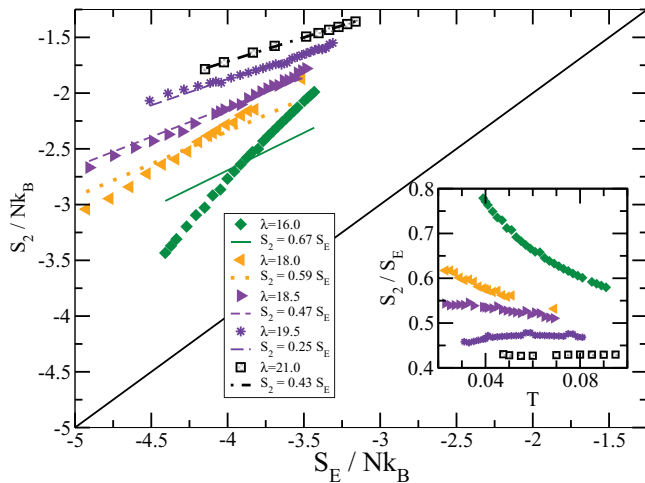


FIG. 4. The pair correlation entropy per particle  $s_2 = S_2/Nk_B$  is compared with the excess entropy per particle  $s_E = S_E/Nk_B$  for the modified Stillinger-Weber models. The lines through data are best fits of the form  $s_2 = ms_E$  and the diagonal solid line represents  $s_2 = s_E$ . Inset: The ratio  $S_2/S_E$  vs. temperature for different  $\lambda$ .

the correlation between the reduced diffusivity  $D^*$  and the pair-correlation entropy  $S_2$  as a function of  $\lambda$ . If the Rosenfeld relation (Eq. (2)) holds between  $D^*$  and  $S_2$ , then  $\ln D^*$  should be linearly correlated with  $S_2$ . We see from Fig. 5 that the linearity of  $\ln D^*$  vs.  $S_2$  is reasonably well observed above the melting temperatures (indicated by vertical lines), albeit with slopes (coefficient  $b$  in Eq. (2)) that are more strongly dependent on  $\lambda$  than in the case of  $S_E$ .

The above-mentioned observations taken together imply that while the diffusivity is well correlated with the excess as well as the pair correlation entropy at all values of  $\lambda$ , the Rosenfeld relation describes data better at higher temperatures and lower  $\lambda$ . Consequently, the validity of the Rosenfeld relation (at least above melting points) immediately suggests that both the excess entropy  $S_E$  and the pair correlation entropy  $S_2$  at constant temperature and pressure should also show maxima as functions of  $\lambda$ . We choose four representative temperatures denoted by horizontal solid lines in Fig. 1 to

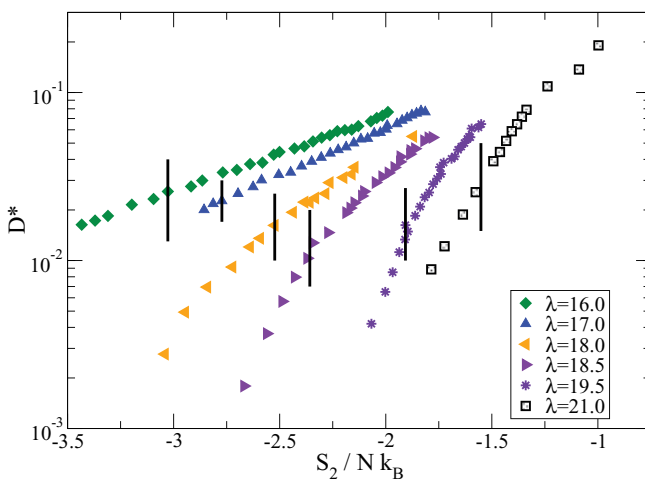


FIG. 5. The plot of the dimensionless isobaric diffusivity  $D^* = \frac{\rho^{1/3}}{(k_B T/m)^{1/2}} D$  vs. the pair correlation entropy  $S_2/Nk_B$  for different  $\lambda$ . Vertical lines denote melting temperatures.

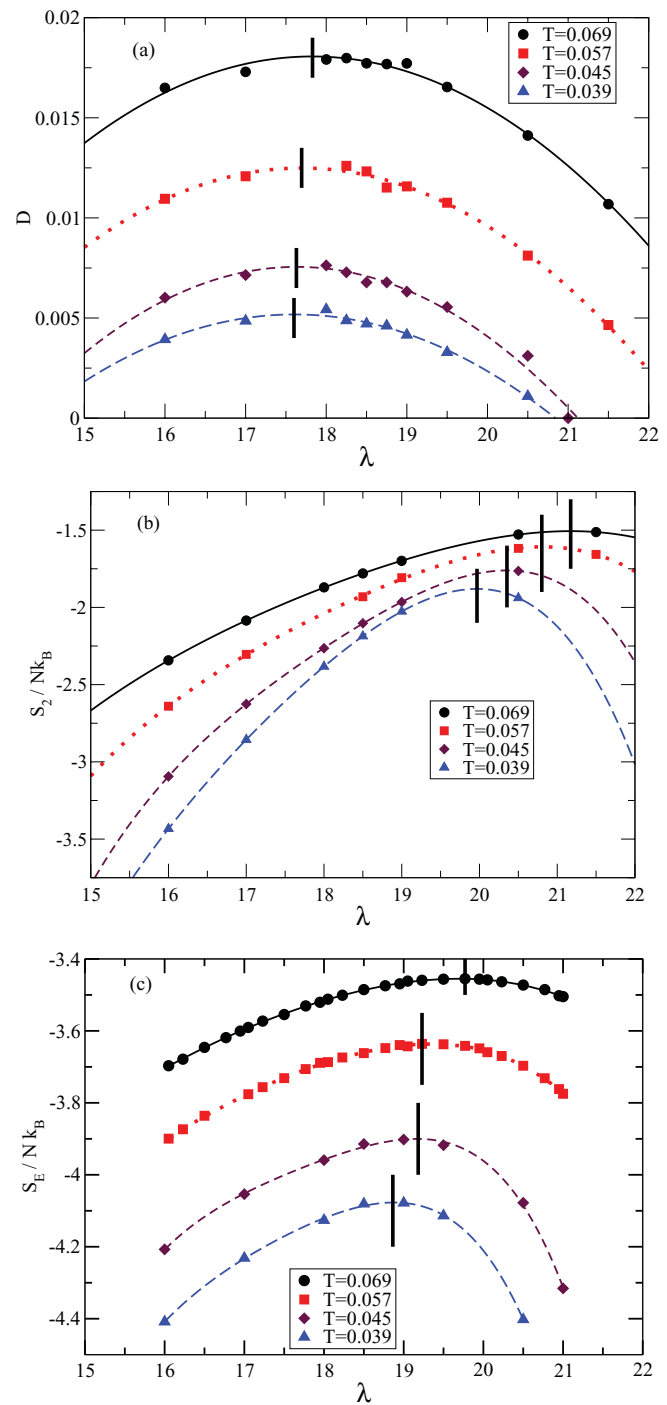


FIG. 6. (a) The isothermal diffusivity, (b) pair correlation entropy  $S_2/Nk_B$ , and (c) excess entropy  $S_E/Nk_B$  vs.  $\lambda$ , go through a maximum at each of the temperatures shown. Lines through data points are polynomial fits. Vertical lines indicate positions of maxima of the fit curves (occurring in the range (a)  $\lambda \approx 17.6-17.8$ , (b)  $\lambda \approx 19.9-20.9$ , and (c)  $\lambda \approx 18.8-19.8$ ). The peaks of excess entropy are closer to those of diffusivity than the peaks of the pair correlation entropy.

study the  $\lambda$  dependence of isothermal diffusivity, pair correlation, and excess entropies. At the highest ( $T = 0.069$ ) of the four temperatures, the system is in liquid phase at all  $\lambda$  except  $\lambda = 21.5$  whereas at the lowest ( $T = 0.039$ ) of the four temperatures, the system is in supercooled liquid phase except in the range  $\lambda \approx 17.5-19.5$ . First, we verify (Fig. 6) that at all the studied temperatures, the isothermal reduced diffusivities

as a function of  $\lambda$  indeed show maxima. The maxima occur in the range  $\lambda \approx 17.6$ – $17.8$  indicating that the temperature dependence of the positions of maxima is weak. Next, Fig. 6 shows that at each of the studied temperatures, a maximum is indeed found for isothermal  $S_2$  and isothermal  $S_E$  as functions of  $\lambda$ . Thus the diffusivity anomaly indeed also has structural and thermodynamic counterparts in the modified Stillinger-Weber model. However, we note that the maxima of isothermal  $S_2$  occur in the range  $\lambda \approx 19.9$ – $20.9$ , i.e., at higher values of  $\lambda$  than that of  $D^*$ , and the temperature dependence of the maximum of  $S_2$  is stronger than that of  $D$ . Compared to the maxima of  $S_2$ , the maxima of the isothermal excess entropy occur relatively closer ( $\lambda \approx 18.8$ – $19.8$ ) to those of isothermal diffusivity  $D^*$ .

## V. SUMMARY AND CONCLUSIONS

We have studied Rosenfeld-like relations between diffusivity and excess as well as pair correlation entropies by tuning the tetrahedrality of interaction in liquids modeled by modified Stillinger-Weber potentials, with the aim of understanding (a) the extent to which structural and thermodynamic changes in these model liquids can help rationalize the diffusivity anomalies observed, and (b) the range in temperature and anisotropy of interactions over which the relationship between diffusivity and entropy is valid. The ability to rationalize anomalous behaviour offers a stringent test for the applicability of semi-empirical relations such as the Rosenfeld relation. We find that, in terms of both the excess and the pair correlation entropy, the Rosenfeld relation describes data better above melting temperature and for more isotropic interactions in the modified Stillinger-Weber liquids. Further we find that the excess and the pair correlation entropies at the same temperatures indeed go through maxima as functions of the interaction potential as expected if the Rosenfeld relation is valid. Below the melting temperatures, the linear dependence of  $\log D^*$  on  $S_E$  (or  $S_2$ ) breaks down. In the high temperature regime, the Rosenfeld scaling relation is valid more convincingly with  $S_E$  than  $S_2$ , with the coefficient  $b$  in the relationship (Eq. (2)) having a modest dependence on the tetrahedrality of interaction  $\lambda$ . Given the fact that the interaction potentials are anisotropic, and the degree of anisotropy is a variable in our study, it is not surprising that  $S_2$  proves to be a poor substitute for excess entropy. Nevertheless, both  $S_E$  and  $S_2$  exhibit anomalous dependence on the tetrahedrality of interaction, and thus show qualitative consistency with the presence of the diffusivity anomaly. In view of the deviations from Rosenfeld scaling below the melting temperature, and the considerable body of work that has explored the validity

of the Adam-Gibbs relation in glass forming liquids, it will be interesting to test whether the Adam-Gibbs relation between the diffusivity and the *configurational* entropy yields a better organization of data as a function of interaction potentials at low temperatures.

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