Breakdown of The Excess Entropy Scaling for the Systems with Thermodynamic Anomalies

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This article presents a simulation study of the applicability of the Rosenfeld entropy scaling to the systems which can not be approximated by effective hard spheres. Three systems are studied: Herzian spheres, Gauss Core Model and soft repulsive shoulder potential. These systems demonstrate the diffusion anomalies at low temperatures: the diffusion increases with increasing density or pressure. It is shown that for the first two systems which belong to the class of bounded potentials the Rosenfeld scaling formula is valid only in the infinite temperature limit where there are no anomalies. For the soft repulsive shoulder the scaling formula is valid already at sufficiently low temperatures, however, out of the anomaly range.

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I. INTRODUCTION

It is well known that some liquids (for example, water, silica, silicon, carbon, and phosphorus) show anomalous behavior in the vicinity of their freezing lines [1–18]. The water phase diagrams have regions where a thermal expansion coefficient is negative (density anomaly), a self-diffusivity increases upon pressuring (diffusion anomaly), and the structural order of the system decreases upon compression (structural anomaly) [3, 4]. The regions where these anomalies take place form nested domains in the density-temperature [4] (or pressure-temperature [2]) planes: the density anomaly region is inside the diffusion anomaly domain, and both of these anomalous regions are inside the broader structurally anomalous region. It is natural to relate this kind of behavior with the orientational anisotropy of the potentials, however, there are a number of studies which demonstrate the water-like anomalies in fluids that interact through spherically symmetric potentials [19–31, 33–45].

It was shown [17, 18] that the thermodynamic and kinetic anomalies may be linked through excess entropy. In particular, in Refs. [17, 18] the authors propose that entropy scaling relations developed by Rosenfeld [46, 47] can be used to describe the regions of diffusivity anomaly.

Rosenfeld based his arguments on the approximations of liquid by an effective hard sphere system. In this approach the kinetic coefficients are expressed in reduced units based on the mean length related to density of the system $d = \rho^{-1/3}$ and thermal velocity $v_{th} = (k_B T/m)^{1/2}$. The reduced diffusion coefficient $D^*$, viscosity $\eta^*$ and thermal conductivity $\kappa^*$ are written in the form

$$D^* = D \frac{\rho^{1/3}}{(k_B T/m)^{1/3}} \quad (1)$$

$$\eta^* = \eta \frac{\rho^{-2/3}}{(mk_B T)^{1/2}} \quad (2)$$

$$\kappa^* = \kappa \frac{\rho^{-2/3}}{(k_B k_B T/m)^{1/2}} \quad (3)$$

Rosenfeld suggested that the reduced transport coefficients can be connected to the excess entropy of the system $S_{ex} = (S - S_{id})/(N k_B)$ through the formula

$$X = a_X e^{b_X S_{ex}}, \quad (4)$$

where $X$ is the transport coefficient, and $a_X$ and $b_X$ are constants which depend on the studying property [47]. Interestingly the coefficients $a$ and $b$ show extremely weak dependence on the material and can be considered as universal.

Another expression for relating diffusion coefficient to the excess entropy was suggested by Dzugutov [49]. In this approach the natural parameters of the system were chosen to be the particle diameter $\sigma$ and the Enskog collision frequency $\Gamma_E = 4\pi^2 [g(\sigma)\rho \sqrt{\pi k_B T}]/m$, where $g(\sigma)$ is the value of radial distribution function at contact. In case of continuous potentials the value of $\sigma$ corresponds to the distance of the first maximum of radial distribution function. Defining the reduced diffusion coefficient as

$$D_D^* = \frac{D_D}{\Gamma_E \sigma^2} \quad (5)$$

where $s_2$ is a pair contribution to the excess entropy [49]. It was shown that this relation holds for many simple liquids. At the same time this equation is not strictly valid for liquid metals. In the work [50] it was shown that in this case it is necessary to replace the pair entropy $s_2$...
by the full excess entropy $S_{ex}$. It was also shown that Dzugutov formula does not work for silica modelled with an angular dependent potential [50]. It allows to say that Rosenfeld relation is more general.

Remember that original idea underlying the Rosenfeld relation is to refer the system under investigation to the hard spheres system. In this respect it is interesting whether the Rosenfeld scaling relation is valid for the systems essentially different from the hard spheres. One of the examples of such systems is the system with potentials with negative curvature [19, 20]. It was shown in many publications that the behavior of such systems is very complex [41, 44, 45, 51, 52]. In particular such systems can form complicated structures, like cluster liquids or different crystal phases. They can demonstrate maximum on the melting line and reentrant melting and many other unusual properties. In particular systems with negative curvature can demonstrate anomalous behavior [17, 26, 30, 32, 59, 45, 58].

It was suggested that the Rosenfeld relations can hold even in the case of anomalous diffusion [17, 18]. For example, in the paper [18] the dependence of both excess entropy and diffusion coefficient on density are reported for the core-softening potential that consists of a combination of a Lennard-Jones potential plus a Gaussian well. This potential can represent a whole family of two length scales intermolecular interactions, from a deep double-well potential to a repulsive shoulder. Accordingly to these dependencies both excess entropy and diffusion have non monotonic behavior which allows to preserve exponential dependence of the diffusion coefficient on the excess entropy. It means that the thermodynamically anomalous regions are characterized by anomalous behavior of the excess entropy which induces anomalous diffusion as well.

Another example of systems which can not be approximated by a hard sphere model is the systems with bounded potentials [50, 61, 62]. Since these potentials have no singularity in the origin the behavior of such system is strongly different from the behavior of hard spheres.

One of the most common model with bounded potential is the Gaussian Core Model (GCM). This system is defined by the potential

$$ U_G(r) = \varepsilon e^{-r^2/\sigma^2}. $$

(6)

This potential was introduced by Stillinger [59] for simulation of the plastic crystals system. The phase diagram of the GCM demonstrates two crystal phases - fcc and bcc [62]. Starting from the densities around $\rho \sigma^3 \approx 0.25$ the melting curve has a negative slope. It was also shown that GCM demonstrates liquid state anomalies: density anomaly [62, 64], diffusion anomaly [64, 65] and structural anomaly [64]. Interestingly Stockes-Einstein relation is also violated in the GCM system [64].

In the article [67] an extensive study of another model with bounded potential was reported. This work is concerned to the Herzian spheres system which is defined by the interparticle potential of the form

$$ \Phi(r) = \begin{cases} \varepsilon(1 - r/\sigma)^{5/2}, & r \leq \sigma \\ 0, & r > \sigma \end{cases} $$

(7)

The phase diagram of the Herzian spheres system demonstrates very complex behavior, including many crystal phases and reentrant melting. Anomalous diffusion is also reported [67].

Taking into account that the behavior of the systems with negative curvature potentials and the systems with bounded potentials is rather different from the behavior of hard spheres a question arises if the Rosenfeld scaling relations are applicable for such systems.

The purpose of this article is to analyze the validity of the entropy scaling for the systems with anomalous behavior. For our analysis we have chosen the diffusion coefficient since it is the simplest transport coefficient to calculate in simulation. The article is organized as follows. In the second section we describe the models investigated in the present work and the simulation setup. Section III gives the results of the simulations and the discussion of these results. Finally the section IV represents our conclusions.

II. THE SYSTEMS AND METHODS

Three systems were studied in the present work: Herzian spheres, Gauss core model and a soft repulsive shoulder system.

For the simulation of the Herzian spheres we used a system of 1000 particles in a cubic simulation box. NVE MD simulation was carried. Equations of motion were integrated by velocity Verlet algorithm. The time step was set to $dt = 0.0005$. The equilibration run was $5 \cdot 10^5$ time steps and the production run $1.5 \cdot 10^6$ time steps. During the equilibration the velocities were rescaled to keep the temperature constant. The diffusions were computed via the Einstein relation for the densities from $\rho = 1.0$ till $\rho = 15.0$ with the step $\Delta \rho = 0.5$. Additional simulations were done for computing the equation of state for the densities less than unity. Free energy of the liquid was calculated by integrating the pressure along an isotherm [68] and the excess entropy was computed via the Einstein relation for the freezing the pressure along an isotherm [68].

In the case of GCM the system consisted of 2000 particles. The time step was set to $dt = 0.05$. The equilibration and production runs were $4 \cdot 10^5$ and $1 \cdot 10^6$ time steps respectively. The diffusion
was computed for the densities from $\rho = 0.1$ to $\rho = 1.0$ with the step of 0.1 for the isotherms $T = 0.04; 0.05; 0.06; 0.07; 0.1; 0.2; 0.3; 0.4; 0.5; 1.0; 2.0$.

The calculation of the diffusion coefficient and excess entropy was carried in the same way as for Herzian spheres.

The last system considered in the present work is the continuous repulsive shoulder system introduced in the article [41]. The potential of this system has the form

$$U(r) = \left(\frac{\sigma}{r}\right)^{14} + \frac{1}{2}\varepsilon \cdot [1 - \tanh(k_0(r - \sigma_1))],$$

where $k_0 = 10.0$. As it was reported in the paper [45] this system demonstrates anomalous behavior due to its quasibinary nature. Here we extend the investigation of the diffusion anomaly in the repulsive shoulder system with $\sigma_1 = 1.35$ and check the Rosenfeld relations for this system in the anomalous region.

For the simulation of the repulsive shoulder system we used parallel tempering technic [68]. The details of the simulation were described in [45]. We computed the diffusion coefficients along different isochors starting from the density $\rho = 0.3$ to $\rho = 0.8$ with the step 0.05. A set of 24 temperatures between $T = 0.2$ and $T = 0.5$ was simulated. Taking into account the exchange of the temperatures at the same density more then a hundred runs at the same isochor was done. This allowed us to collect a good statistics on the temperature dependence of the diffusion coefficient. The diffusion coefficient along an isochor was approximated by a 9-th order polynomial of the temperature. The excess entropy was calculated in the way described above.

Usually excess entropy can be well approximated by the pair contribution only: $S_{ex} = S_{\text{pair}} + S_3 + \ldots \approx S_{\text{pair}}$, where

$$S_{\text{pair}} = -\frac{1}{2} \rho \int d\mathbf{r} [g(\mathbf{r}) \ln(g(\mathbf{r})) - (g(\mathbf{r}) - 1)],$$

where $\rho$ is the density of the system and $g(\mathbf{r})$ is the radial distribution function. We did not use the pair contribution to the excess entropy for the GCM and Herzian spheres because of the considerable overlap of the particles for the bounded potentials.

Since the potentials studied in the present work have negative curvature regions or are bounded they can not be approximated by an one component hard spheres system. It allows us to pose a question about the applicability of the entropy scaling to these systems both in Rosenfeld and Dzugutov forms. Note that Dzugutov relation (Eq. (5)) involves the size of the particles $\sigma$ which is ill defined for the negative curvature and bounded potentials systems. This makes problematic to apply the Dzugutov scaling rule to them. Because of this only Rosenfeld relations were used in this work.

In this paper we use the dimensionless quantities: $\mathbf{r} = \mathbf{r}/\sigma$, $\tilde{P} = P\sigma^3/\varepsilon$, $\tilde{V} = V/N\sigma^3 = 1/\tilde{\rho}$, $\tilde{T} = k_BT/\varepsilon$. Since we use only these reduced units we omit the tilde marks.

## III. RESULTS AND DISCUSSION

This section reports the simulation results for the diffusion coefficient and excess entropy of the three models described above and checks the validity of the Rosenfeld relation for these systems.

### Herzian spheres

Low temperature behavior of the diffusion coefficient of Herzian spheres system was already reported in the work [67]. As it is seen from this publication the diffusivity shows even two anomalous regions at the temperature $T = 0.01$ where diffusion coefficient grows with growing density. In the present work the dependence of the diffusion coefficient on density along several isotherms was monitored. The simulation data are presented on the Fig. 1 (a) - (b).

One can see from these figures that at low temperatures (Fig. 1(a)) the diffusion is non monotonic, while at high temperatures it monotonically decays with increasing density (Fig. 1(b)) and comes to a constant value (see inset of the Fig. 1(b)).

It is worth to note that the melting temperatures of Herzian spheres reported in the work [67] are of the order of $10^{-3}$, so the temperatures about 0.1 are extremely high for this model. This is easily seen from the Fig. 2(a) - (b) where the radial distribution functions for the density $\rho = 6.0$ are shown for the same set of temperatures. One can see that at $T = 0.01$ the liquid has short range structure which rapidly decays with increasing temperature. At the temperature $T = 0.1$ the liquid looks almost like an ideal gas since $g(\mathbf{r})$ comes to unity very quickly.

Excess entropy also shows non monotonic dependence on density along an isotherm (Fig. 3(a) -(b)). One can see from these figures that at low temperatures excess entropy has two minima and a maxima in the investigated density range while at high temperature the first minima is depressed and the curves just change the slope smoothly.

Now we turn to the Rosenfeld relation for the Herzian spheres system. The dependence of the reduced diffusion (see formula (1)) on the excess entropy along some isotherms is shown in the Fig. 4 (a) - (b). Looking at the curve for $T = 0.01$ (Fig. 4 (a)) one can divide it into three distinct regions with different slopes which we denote as ‘1’, ‘2’ and ‘3’. The density increase corresponds to moving along the curves from right to left, i.e. region 2 corresponds to the higher densities then 1, and 3 - higher densities then 2. As is seen from the plots the region 3
rapidly disappears with increasing the temperature. Already at $T = 0.03$ this region is negligibly small. Recall from the figures 1 and 3 that at low temperatures both diffusion and excess entropy behave non monotonically while at growing the temperature this effect disappears. This leads to the depression of the region 3 in the Fig. 4 (a).

The region 2 is rather stable. As one can see from the Fig. 4 (b) this region also becomes less developed with increasing the temperature, but it still preserves even for high temperatures. It makes the excess entropy scaling curve consisting from two parts of different slope and a cross region.

Fig. 5 summarizes all the results obtained for Herzian spheres system. Ten different isotherms are shown there. As one can see only at the temperature as high as 0.5 the Rosenfeld linear relation between the logarithm of the reduced density and the excess entropy becomes valid. Remember that the melting temperature is of the order of 0.005, that is 100 times smaller. It allows to say that the Rosenfeld relation for diffusion coefficient of Herzian spheres is valid only in the infinitely high temperature limit.
Gaussian Core Model

The results for the GCM are qualitatively similar to the case of Herzian spheres. Because of this we do not explain them in detail. Fig. 6(a) and (b) shows the diffusion coefficient for the GCM system for a set of six isotherms. One can see that for low temperatures starting from the densities approximately 0.3 the diffusion coefficient demonstrate anomalous growth with increase of the density. We expect that at higher densities the curve bends downward but in the present study we have not measured so high densities for this model. At high temperatures the diffusion monotonically decreases with increasing the density.

The structure of the liquid rapidly decays with the temperature increase. This is shown in the Fig. 7(a) - (b). One can see that at the temperature $T = 1.0$ $g(r)$ is equal to unity almost in the whole range of the distances $r$.

Like the diffusion coefficient the excess entropy has a minimum at the low temperatures, but with increasing the temperature it becomes monotonically decreasing function of the density (Fig. 8(a) - (b)).

Fig. 9(a) - (b) demonstrates the Rosenfeld relation for the GCM for the same set of isotherms. Comparing to

FIG. 3: Excess entropy along and a set of isotherms. (a) - $T = 0.01; 0.02$ and $0.03$; (b) - $T = 0.1; 0.2$ and $0.3$.

FIG. 4: The dependence of reduced diffusion on the excess entropy (see formulas (1) and (4)) along some isotherms (a) - $T = 0.01; 0.02$ and $0.03$; (b) - $T = 0.1; 0.2$ and $0.3$. 
the case of Herzian spheres there is no region '3' in the low temperature curves of the GCM. We suppose that this region corresponds to the higher densities which we do not consider in the present study. At low temperatures most of the points belong to the region '2'. However this region depresses with the temperature increase. Although even at the temperature as high as \( T = 2.0 \) which is around 200 times higher then melting temperature of GCM the curve still demonstrates a bend from a straight line at high densities.

Finally Fig. 10 shows the whole set of isotherms investigated in the present study. As one can see from this figure the system comes more close to the Rosenfeld relation with increasing the temperature. One can expect that at infinitely high temperatures the excess entropy relation is valid for the GCM, however in the temperatures range studied here, i.e. to approximately 200 \( T_{mels} \) a deviation from the linear behavior is still observed.

**Soft Repulsive Shoulder Model**

The last model considered in the present work is the soft repulsive shoulder potential \( (8) \). In the works \[41, 45\] it has already been shown that this system demonstrates anomalous behavior of diffusion at low temperatures and densities corresponding to the region where a competition between the characteristic length scales \( \sigma \) and \( \sigma_1 \) takes place. This competition gives the great complexity of the phase diagram of the system \[41, 45\], so one can expect that the thermodynamic quantities, in particular entropy which is of the interest of the present study, also have a complex behavior in this region of densities. Taking into account the complex behavior of both entropy and diffusion coefficient it is interesting to check the Rosenfeld relation for this system.

Fig. 11 represents the diffusion coefficient for the soft repulsive shoulder system with \( \sigma_1 = 1.35 \) for a set of temperatures and densities. One can see that at \( T = 0.25 \) an inflection point in the diffusion coefficient curve occurs which then develops into a loop \( (T = 0.2) \).

Both pair and full excess entropies were considered for this potential. Fig. 12 (a) and (b) show the behavior...
FIG. 7: Radial distribution functions of GCM for a set of isotherms at the density $\rho = 0.5$ (a) - $T = 0.04; 0.07$ and 0.1; (b) - $T = 0.5; 1.0$ and 2.0.

FIG. 8: Excess entropy of GCM for a set of isotherms. (a) - $T = 0.04; 0.07$ and 0.1; (b) - $T = 0.5; 1.0$ and 2.0.

of the entropies along two isotherms. One can see that both at high and low temperature the difference between excess entropy and pair contribution to it is rather large. This discrepancy is small at low densities, but greatly increases at the density about 0.4. Note that this density corresponds to a character distance $l \sim \frac{1}{\rho^{1/3}} \simeq 1.35$, that is $l \simeq \sigma_1$. It allows to conclude that the interplay of the distances starts at this density and it is this interplay which makes the excess entropy and pair excess entropy difference to increase rapidly.

Fig. 13 shows the diffusion coefficient scaling with the pair part of the excess entropy. As is seen from the figures even at high temperatures the curve is not straight while at low temperatures the curve becomes very strange. Definitely the exponential relation between the diffusion coefficient and pair excess entropy is not valid.

The diffusion scaling with the full excess entropy is shown in the figure 14 (a) and (b). One can see from these pictures that the scaling rule works good for the temperatures $T = 0.5$ and $T = 0.4$ but already for $T = 0.35$ the deviation from the linear behavior occurs. This deviation develops more as the temperature decreases. At $T = 0.25$ a self crossing loop occurs. This loop even enlarges at lower temperatures. It is worth to note that the curve at low temperature $T = 0.2$ consists of two linear
FIG. 9: Excess entropy of GCM for a set of isotherms. (a) - $T = 0.04; 0.07$ and $0.1$; (b) - $T = 0.5; 1.0$ and $2.0$.

In order to see the reason for the occurrence of the self crossing loop we compare the qualitative behavior of the diffusion coefficient and excess entropy. For this reasons we measure the densities corresponding to the minimum and maximum of the diffusion ($\rho_{D_{\text{min}}}^D$ and $\rho_{D_{\text{max}}}^D$ correspondingly) and excess entropy ($\rho_{S_{\text{min}}}^S$ and $\rho_{S_{\text{max}}}^S$) at the lowest temperature we study $T = 0.2$. The values we obtain are: $\rho_{D_{\text{min}}}^D = 0.44$, $\rho_{D_{\text{max}}}^D = 0.55$, $\rho_{S_{\text{min}}}^S = 0.40$ and $\rho_{S_{\text{max}}}^S = 0.535$. One can see that there is a mismatch in the location of the extremal points of these two quantities and therefore there are some regions where the qualitative behavior of diffusion and excess entropy is opposite. Taking into account exponential dependence supposed in the Rosenfeld formula one can expect that even small discrepancies in the qualitative behavior can lead to large errors in the scaling relation.

FIG. 10: Reduced diffusion coefficient (formula (1)) of GCM for a set of eleven isotherms.

FIG. 11: Diffusion coefficient for soft repulsive shoulder system with $\sigma_1 = 1.35$ along several isotherms. The inset enlarges the isotherms $T = 0.5$ (squares) and $T = 0.25$ (circles).
FIG. 12: Excess entropy and pair excess entropy for the soft repulsive shoulder system for (a) $T = 0.5$ and (b) $T = 0.2$.

FIG. 13: The diffusion scaling with the pair contribution to the excess entropy at (a) high and (b) low temperatures for the soft repulsive shoulder system.

CONCLUSIONS

This article presents a simulation study of the applicability of the Rosenfeld entropy scaling to the systems with negative curvature and bounded potentials. It was shown that the excess entropy scaling can not be applied to such systems at low enough temperatures. Interestingly all of the systems considered here demonstrate anomalous diffusion behavior in some regions of temperatures and densities. It makes questionable if the Rosenfeld relation is applicable for the systems with diffusion anomaly. These results are in contradiction with the results of Refs. [17, 18]. This contradiction may be attributed to the differences of considered potentials and simulation methods, however, this question requires further investigation and will be a topic of a subsequent publication.

One can suppose that the excess entropy scaling is invalid for the systems with negative curvature potentials such as repulsive shoulder potential. A possible reason for this can be related to the fact that such systems are effectively quasibinary [41, 42]. As it was mentioned in the introduction, the original Rosenfeld idea was based on the connection of a liquid under investigation to the effective hard spheres liquid. At the same time liquids with negative curvature potentials may be approximated
FIG. 14: The diffusion scaling with the excess entropy at (a) high and (b) low temperatures for the soft repulsive shoulder system.

by a mixture of hard spheres of two different sizes. The concentration of components of such mixture is pressure and temperature dependent. As it was shown in literature (see, for example, [69]) the excess entropy scaling holds for binary mixtures too. But in the case of quasibinary mixture since the effective concentration depends on the pressure and temperature the behavior becomes more complex. This brings to the breakdown of the scaling rules for this case.

Obviously, the systems with bounded potentials can not be approximated by hard sphere potentials too. It seems that this may be the reason of violation of Rosenfeld entropy scaling for these systems.

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