

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

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This articles 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) [6, 7]. The regions where these anomalies take place form nested domains in the density-temperature [6] (or pressure-temperature [7]) 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 the regions of diffusivity anomaly.

Rosenfeld based his arguments on the approximations of liquid by an effective hard spheres 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 η^* and thermal conductivity κ^* are written in the form

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

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

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

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

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

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 Dzугutov [49]. In this approach the natural parameters of the system were chosen to be the particle diameter σ and the Enskog collision frequency $\Gamma_E = 4\sigma^2 g(\sigma) \rho \sqrt{\frac{\pi k_B T}{m}}$, where $g(\sigma)$ is the value of radial distribution function at contact. In case of continuous potentials the value of σ corresponds to the distance of the first maximum of radial distribution function. Defining the reduced diffusion coefficient as $D_D^* = \frac{D}{\Gamma_E \sigma^2}$. Dzугutov suggested the following formula for it

$$D_D^* = 0.049 e^{s_2}, \quad (5)$$

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