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Liquid State Anomalies in the Gaussian Core Model Liquid

1. Introduction

The well known anomalies of liquid water, like the density maximum at 4°C and 1 bar, are attributed to the occurence of a spacially open network of strongly directional hydrogen bonds. But interestingly enough, a most simple fluid, the Gaussian core model (GCM) [1] with radial, pair additive interactions of the form

$$\phi(r_{ij}) = \phi_0 \exp\left[-(r_{ij}/l)^2\right],$$

also exhibits a line of density maxima in the p,T–plane (temperature of maximum density line TMD). In [2] we specified the course of this line, which shows waterlike features. In the present contribution we examine the response functions thermal expansivity α_p, constant pressure specific heat C_p and isothermal compressibility κ_T. In supercooled water these properties show an anomalous behaviour, which has been explained recently by the second critical point hypothesis of Stanley et al. [3].

2. Results and discussion

We start from the p, V, T– data of the GCM fluid, obtained by an extensive molecular dynamics study [2]. To these data an equation of state (EOF) of third order polynomials is fitted, from which the response functions α_p, κ_T and C_p are derived then.

The thermal expansivity $\alpha_p = -v^{-1} (\partial v/\partial T)_p$ describes the specific volume response δv to a temperature change δT. α_p is determined by cross fluctuations of specific volume and entropy $< \delta v \delta S >$. In ordinary liquids, local fluctuations which increase the volume result in increased local entropy contributions, leading to a positive expansion coefficient α_p. Fig. 1a gives α_p in reduced units as function of reduced density and temperature. For large temperatures the GCM shows normal behaviour ($\alpha_p > 0$), but at lower temperatures and medium to high densities we observe in analogy to liquid water an anomalous behaviour ($\alpha_p < 0$). The α_p surface in Fig. 1a is slightly distorted by oscillations, which stem from the polynomial approximation to the EOS, but the general behaviour of α_p is not influenced by this artefact.

The isothermal compressibility $\kappa_T = v^{-1} (\partial v/\partial p)_T$ describes the thermodynamic response δv of the specific volume to a pressure change δp. κ_T is related to the volume fluctuations $< (\delta v)^2 >$. Usually, these fluctuations diminish with decreasing temperature. In water this quantity behaves anomalously by passing a minimum at 46°C and increasing dramatically in the supercooled liquid. In Fig. 1b κ_T of the GCM liquid is shown as a function of density and temperature. A water–like temperature anomaly can not be observed in the large temperature and density range investigated here.

From α_p and κ_T the difference of the specific heats at constant pressure and constant volume can be obtained by the following thermodynamic identity

$$C_p - C_V = vT\alpha_p{}^2/\kappa_T .$$

This quantity is shown in Fig. 1c. As $\alpha_p = 0$ along the TMD–line, which we obtained in [2], the locus of minima exhibited by this surface follows the same line. The specific heat C_V can be obtained from the internal energy U, which is also calculated during the simulation runs ($C_V = (\partial U/\partial T)_V$). And in combination with the above formula, C_p can be calculated. The temperature dependence of C_p at different densities is shown in Fig. 1d. C_p is determined by entropy fluctuations $< (\delta S)^2 >$ and decreases monotonically with temperature in normal liquids. In contract to this and in agreement with the anomalous behaviour of water, C_p of the GCM increases with decreasing temperature.

In conclusion, the GCM fluid shows several, but not all of the anomalies of water, especially those which are determined by entropy fluctuations. This should be a consequence of the softness of the repulsive core with a negative curvature of the interaction potential at close encounters. By this, a decrease of the volume may lead to an increase of the accessible phase space [1].

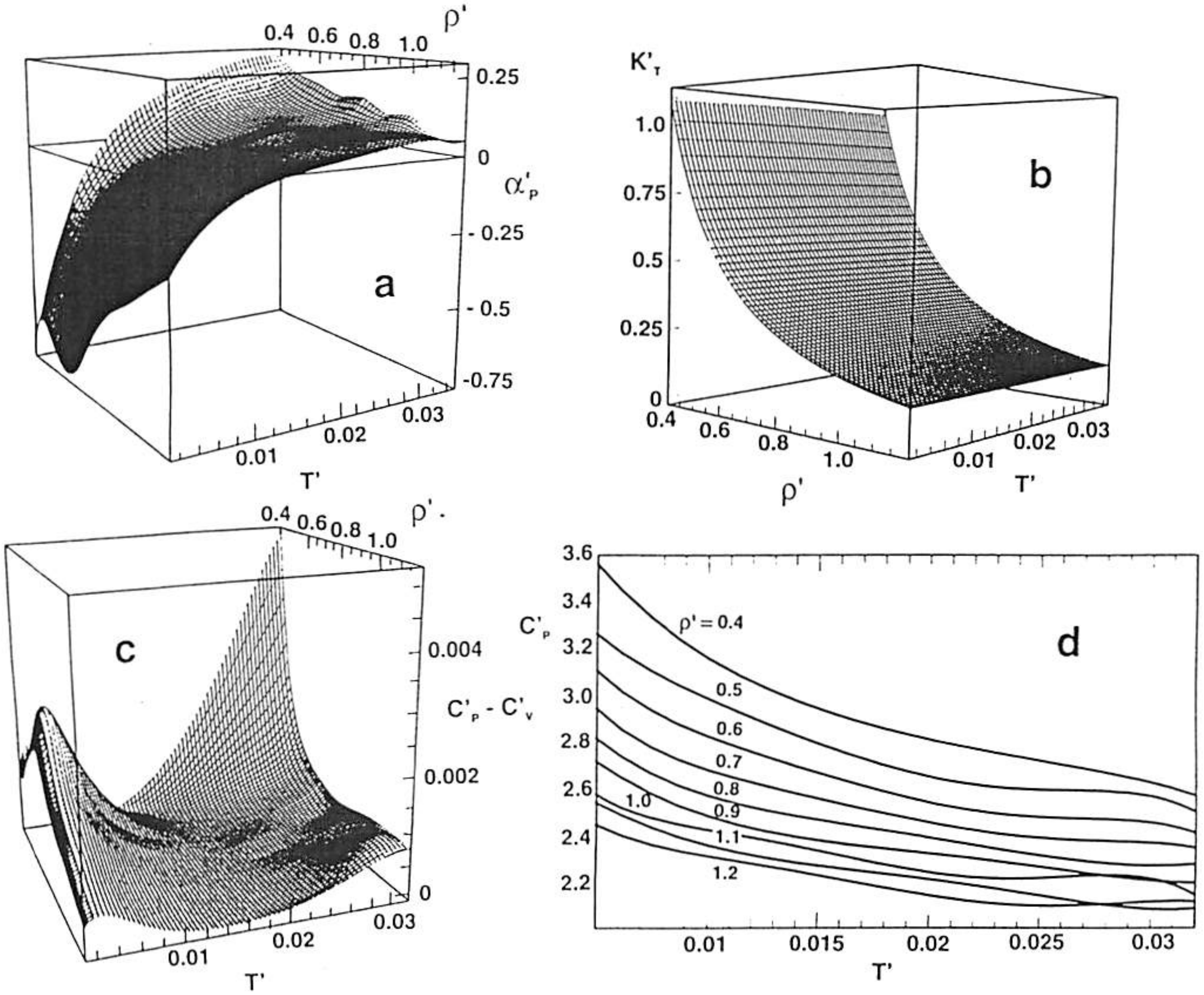

Figure 1: *(a)*: Thermal expansion coefficient α_p', *(b)*: isothermal compressibility κ_T', *(c)*: $C_\mathrm{p}' - C_\mathrm{V}'$, and *(d)*: constant pressure specific heat C_p' as functions of density ρ' and temperature T'.

All quantities are given in reduced units:

$$\alpha_\mathrm{p}' = \alpha_\mathrm{p}\phi_0 / k_\mathrm{B}\,,\ \kappa_\mathrm{T}' = \kappa_\mathrm{T}\phi_0 / l^3,\ C_\mathrm{p}' = C_\mathrm{p} / k_\mathrm{B}\,,\ \rho' = N l^3 / {L_\mathrm{B}}^3\,,\ T' = k_\mathrm{B} T / \phi_0\,.$$

Here, ϕ_0 and l are the height and width of the GC interaction profile, k_B the Boltzmann constant, L_B the edge length of the simulation box, and N the number of particles in this box.

3. References

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