Heterogeneities in Supercooled liquids: A Density Functional Study

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Abstract

A metastable state, characterized by a low degree of mass localization is identified using Density Functional Theory. This free energy minimum, located through the proper evaluation of the competing terms in the free energy functional, is independent of the specific form of the DFT used. Computer simulation results on particle motion indicate that this heterogeneous state corresponds to the supercooled state.

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The properties of supercooled liquids are of much current interest and are being studied from different approaches related to their thermodynamic as well as dynamic aspects [1]-[6]. A normal liquid is characterized by a homogenous density and when it is supercooled below the freezing transition it continues to stay in the amorphous phase. With the increase in density a solid like phase is formed with the particles being localized around their mean positions on a random structure. The underlying lattice on which such localized motion takes place is related to the time scales of relaxation in the supercooled liquid. While the supercooled liquid starts to attain solid like properties, structurally it does not have any long range order like the one present in a crystal. The Heterogeneity in glassy systems over length and time scales has been studied in several recent works, [7], related to computer simulations. Here we consider the heterogeneous density profile in the liquid and investigate the question of having metastable states in between the homogeneous liquid state and the regular crystalline state. The stability of such a structure has been studied in this work from a thermodynamic point of view, using the standard methods of Density Functional Theory (DFT). It provides the means to test if a given structure i.e. a configuration of atoms is the "most" stable at a specified temperature and density. This method has generally been used [8]-[12] for the study of a liquid freezing into an ordered crystalline state through a first order transition.

In practical calculations of the DFT an explicit functional form for the inhomogeneous density function against which the Free energy functional is tested, is needed. One very successful prescription of density distribution is as a superposition of density profiles centered on a Lattice,

$$\rho(\vec{r}) = \sum_i (\frac{\alpha}{\pi})^{\frac{3}{2}} e^{-\alpha|\vec{r}-\vec{R}_i|^2}. \tag{1}$$

where the $\{\vec{R}_i\}$ denotes the underlying lattice. Here α is the variational parameter that characterizes the width of the peak, which represents the degree of localization of mass in the system. Thus the homogeneous liquid state is characterized by Gaussian profiles of very large width such that each provides the same contribution in the sum at all spatial positions. Singh *et.al.* [13] have shown that the distribution of $\vec{R}_i$ over a random lattice determined from the Bernal packing [14] allows a metastable minimum for the free energy functional for packing fraction η beyond .59. This is obtained for very large α, that corresponds to an inhomogeneous and *highly localized* density distribution that has been termed as the "hard sphere glass". This metastable state however is not compatible with the experimental findings [5, 6] which find the metastable supercooled state with a much lower degree of localization.

We have studied this through the various [8, 11] formulations of the DFT for the density profiles centered around a random lattice that corresponds to a heterogeneous density distribution. Here we consider the density profiles that are *less* localized than the so-called hard sphere glass by evaluating the Free energy of the system for α values that are *considerably smaller* than what was previously studied. We also consider the effects of fluctuations in the width around a mean value. The key result of this study is the observation of a free energy minimum where the density function corresponds to the small α region. This minimum is seen apart from the usual high α minimum, as reported in the earlier works, [13, 15, 16] and this state can be reached in a *continuous* path from both the liquid and the high α state on the free energy landscape.

The expression for the total free energy contains two parts - the ideal gas term and the interaction term, $F[\rho] = F_{id}[\rho] + F_{ex}[\rho]$. The ideal gas term of the free energy functional (in units of β^{-1}) is given by,

$$F_{id}[\rho] = \int d\vec{r}\rho(\vec{r})(ln[\wedge^3\rho(\vec{r})] - 1) \tag{2}$$

$\wedge$ being the thermal wavelength. In the earlier works, [13, 15, 16], where highly localized structures have been investigated, generally α was chosen to be large (greater than ≈ 50)

and eqn.(2) was approximated by its asymptotic value for large α,

$$F_{id}[\rho] \approx N[-\frac{5}{2} + ln(\wedge^3(\frac{\alpha}{\pi})^{\frac{3}{2}}] \tag{3}$$

However, in the low α range where overlapping Gaussians from different sites contribute, we evaluate this term exactly from the computation of the integral given in (2) as,

$$f_{id}[\rho] = \int d\vec{r}\phi(\vec{r}) \left[ln \left(\wedge^3 \int d\vec{R}\phi(\vec{r} - \vec{R}) \left(\delta(\vec{R}) + \rho_o g(\vec{R}) \right) \right) - 1 \right] \tag{4}$$

where $g(\vec{R})$ is the site-site correlation function which provides the structural description of the random structure used. We have used the Bernal's random structure [14] generated through the Bennett's algorithm [17]. We approximate the $g(\vec{R})$ as,

$$g(\vec{R}) = g_B[R(\frac{\eta}{\eta_o})^{\frac{1}{3}}] \tag{5}$$

where η denotes the average packing fraction and η_o is used as a scaling parameter for the structure, [15, 16] such that at $\eta = \eta_o$ Bernal's structure is obtained. The ideal free energy value evaluated using this exact treatment, eqn.(4), is shown in Figure 1 for $\rho_o = 1.0$. This agrees on extrapolation to the limit of $\alpha \rightarrow 0$ (i.e. $\rho(\vec{r}) \rightarrow \rho_o$) result *i.e.* -1. The exact evaluation starts approaching the asymptotic (large α) result (dashed line), for $\alpha > 20$ within 5% as shown in the figure. The interaction part is evaluated using the standard formalism used by Singh et. al. [13] with the expression for the Ramakrishnan-Yussouff (RY) functional,

$$\Delta F_{ex} = -\frac{1}{2} \int d\vec{r}_1 \int d\vec{r}_2 c(|\vec{r}_1 - \vec{r}_2|; \rho_o) \; \delta\rho(\vec{r}_1) \; \delta\rho(\vec{r}_2) \tag{6}$$

that gives the difference in the free energies of the solid and liquid phase of average density ρ_o. Here $\delta\rho(\vec{r})$ is the density fluctuation from the average value ρ_o. We use the solution of the Percus Yevick equation with Verlet Weiss correction for the direct correlation function, c(r) [18, 19]. The low α minimum becomes a metastable state between the homogeneous liquid state ($\alpha \rightarrow 0$) and the crystal state beyond $\eta = 0.576$ ($\rho_o = 1.10$). In order to clarify this point we have shown in Figure 2, the minimum value for the difference of the free energy per particle (for the corresponding α value) against the density. The Free energy corresponding to the "hard sphere glass" state become metastable w.r.t homogeneous liquid state at average density $\rho_o = 1.14$ [13]. Moreover, the new minimum found in the strongly overlapping region (low α) can be reached continuously from both the liquid state minima and the hard sphere glass state. We also like to stress here that the expansion (6) for the Free Energy of the liquid used in the RY approach is a better approximation for the minima observed at low α than in the case of the highly localized structure called the hard sphere glass. In figure 3, we show the free energy evaluated with the density function obtained for alpha extending to small values. The minimum appears at $\alpha \approx 18$ for ρ_o 1.12. The free energy minimum identified in Ref. [13] also occurs but for very high value of α and corresponds to highly localized structures referred to as the hard sphere glass. The Free energy corresponding to the low α minima is less than that for the "hard sphere glass" state over the density range considered here. However, if the back ground lattice is taken as a *regular* crystalline one then the free energy *does not* show any minimum in the small α region unlike the case of an underlying amorphous structure. This indicates an inhomogeneous structure of strongly overlapping Gaussians centered around regular lattice sites is ruled out. Indeed such uniform structures are never seen in simulations. This *minimum is only seen for the amorphous structure* which signifies a heterogeneous density distribution. This can be given a more quantitative form in the following way : The α corresponding to the minimum free energy value is inversely proportional to the root mean square displacement of the particles from their sites, which also defines the Lindemann [20] ratio. The two minima with the random structure for low and high value of α, respectively found in the present work and in Ref. [13, 15, 16] correspond to very different degrees of localization of the particles. The simulation results, [5, 6], show that the Lindemann ratio of supercooled liquid is approximately three times that of crystal at freezing(Figure 2 of [5]). We have observed a similar relation for the metastable state corresponding to the small α minimum. This is shown in the Figure 4 where we plot the respective root mean square displacement ($d \sim \frac{1}{\sqrt{\alpha}}$) for both the supercooled and the crystal case. This fact strengthens the case for identifying it with the supercooled state seen in computer simulations as compared to the highly localized hard sphere glass which shows a level of localization close to that of the corresponding crystal. The Barrier height between the liquid and the supercooled phase grows with the increase in the average density, as shown by points in the Figure 5. It follows a power law increase with the height diverging at packing fraction ≈ 0.62 and exponent 1.57 as shown by the solid line in the Figure 5. In all these calculations we have used $\eta_o \; = .64$. The pressure (P) and Bulk modulus (E) of the corresponding structure are computed using the first and second derivatives of the total free energy per unit volume ([16]). We show in figure 6, results computed using the present model, for a random structure corresponding to $\eta_o = .68$ in (5). The total free energy is calculated using the Modified Weighted Density Approx (MWDA) treatment [11] with a semi-empirical form of c(r) [21].

We have also considered the fluctuation of the Gaussian Density profile's width parameter α over different sites in the random lattice to incorporate higher degree of heterogeneity. This is modeled by attaching an independent probability distribution function, $P(\alpha_i)$, *to each lattice site*, that governs α value. We chose P to be Gaussian peaked at $\bar{\alpha}$ and spread (half width) $\bar{\alpha}r$, to compute the free energy averaged over the α fluctuations as a function of the parameters $\bar{\alpha}$ and r. These fluctuations in α bring about an overall increase in the free energy of the system i.e. the system stability decreases on account of increased heterogeneity at the individual unit of mass concentration. This is also self consistent with the choice of using the direct correlation function of a hard sphere system with single size.

The motivation of this study has been to evaluate the stability of heterogeneous density distributions from a purely thermodynamic viewpoint. The existence of the free energy minimum corresponding to a density distribution of overlapping Gaussians centered around an amorphous lattice depicts the supercooled state with a heterogeneous density profile. This state can be reached continuously from the homogeneous liquid state or the so-called hard sphere glass minimum. As the density increases the energy barrier to come out of this minimum grows. The identification of this inhomogeneous state is indeed linked to the proper evaluation of the ideal gas part of the free energy. In earlier works this was generally approximated by the asymptotic formula given in equation (3) which works well for large values of α representing highly localized structures. In the present work with the proper evaluation of the ideal gas term for the heterogeneous density, role of configurational packings on the Free energy is taken into account. From our comparison with the Lindemann parameter values (Fig. 4) it follows that this heterogeneous state with less degree of mass localization does agree with the computer simulation results better, as compared to the so called Hard Sphere Glass observed by Singh et. al. [13]. This new minimum does not occur for the structure centered on an ordered lattice like the f.c.c., strengthens the case for the heterogeneous glassy phase.

The qualitative nature of the state is different from the hard sphere glass state that was identified in the earlier works. We have used here the Bernel packing to define the underlying lattice but these studies can be extended to different types of random structure, even taking results from Computer simulation studies. We also like to mention that this new minimum shows up for different forms of the Density functional Theory and with different direct correlation functions. This minima is observed with both the treatments of RY functional and the MWDA [11] even with the PY c(r) without any tail. Indeed improvement of these results can be obtained with a better input for the structure functions using improved techniques [22]. Including higher order correlations namely the three point functions, in the expression (6) is also expected to account for increased cooperativity at high density.

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Figure Captions

Fig 1 : Ideal gas part of the free energy per particle (in units of β^{-1}) vs. α (in units of σ^{-2}) for density ${\rho_o}^* = 1.0$. The solid line is obtained from the exact evaluation, i.e. eqn. (4) and the dashed line is the result from the approximation.

Fig 2 : Free Energy difference per particle (Δf) (in units of β^{-1}) vs. density in the low α regime.

Fig 3 : Difference in Free Energy per particle (Δf) (in units of β^{-1}) vs. α (in units of σ^{-2}) in the low α regime (${\rho_o}^* = 1.12$). The inset demonstrates the continuity of the curve near the maximum.

Fig 4 : Average displacement d (in units of σ) vs. ρ_o. The dashed curve depicts the supercooled phase and the solid line is for the fcc crystal.

Fig 5: Barrier height h (in units of β^{-1}) between the liquid and the supercooled phase vs. the average packing fraction η. The solid line is a power law fit to this data.

Fig 6: The Bulk Modulus E(in units of $(\beta\sigma^3)^{-1}$) vs. density for the amorphous structure. In the inset, pressure P (in units of $(\beta\sigma^3)^{-1}$) vs. density is shown.

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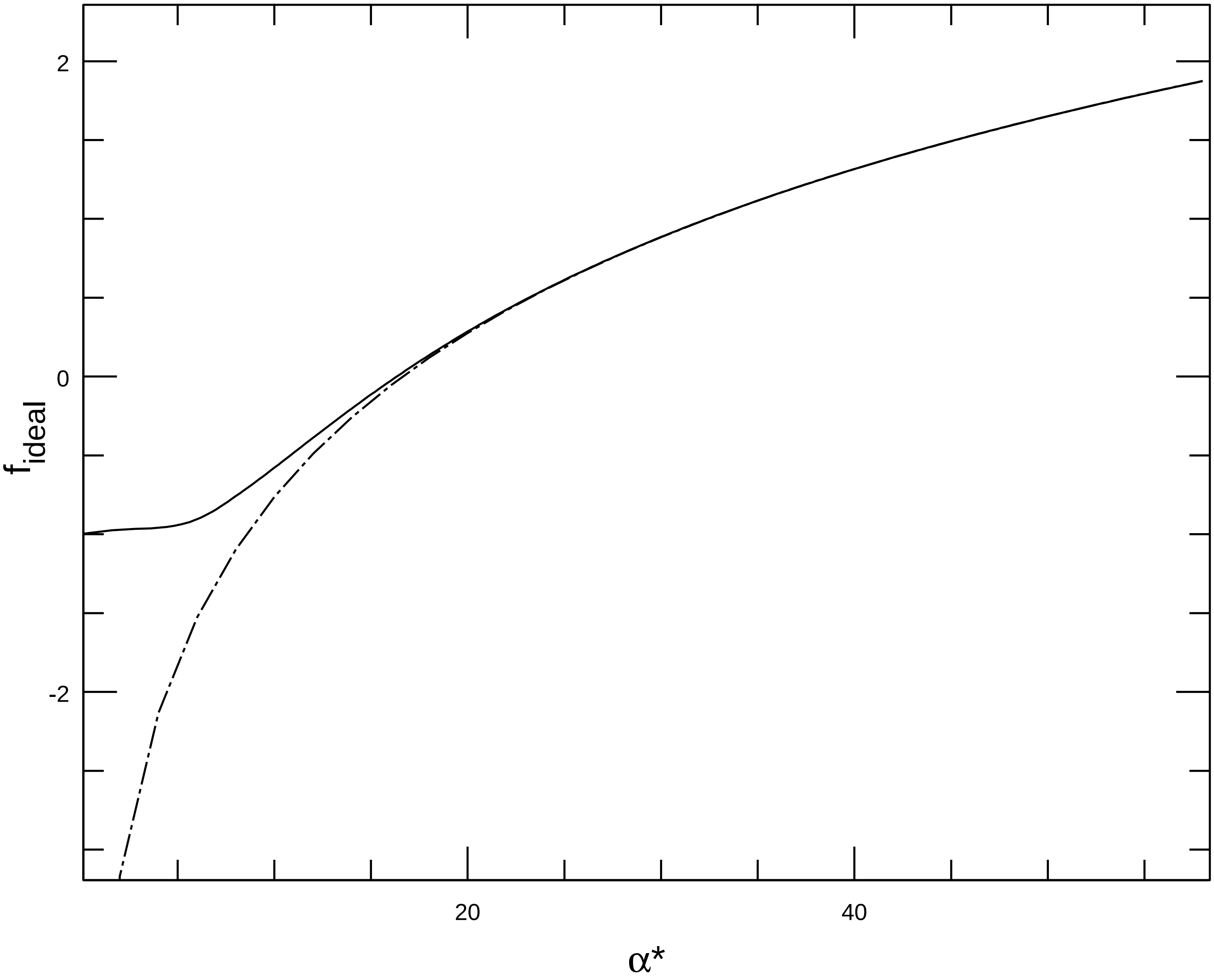
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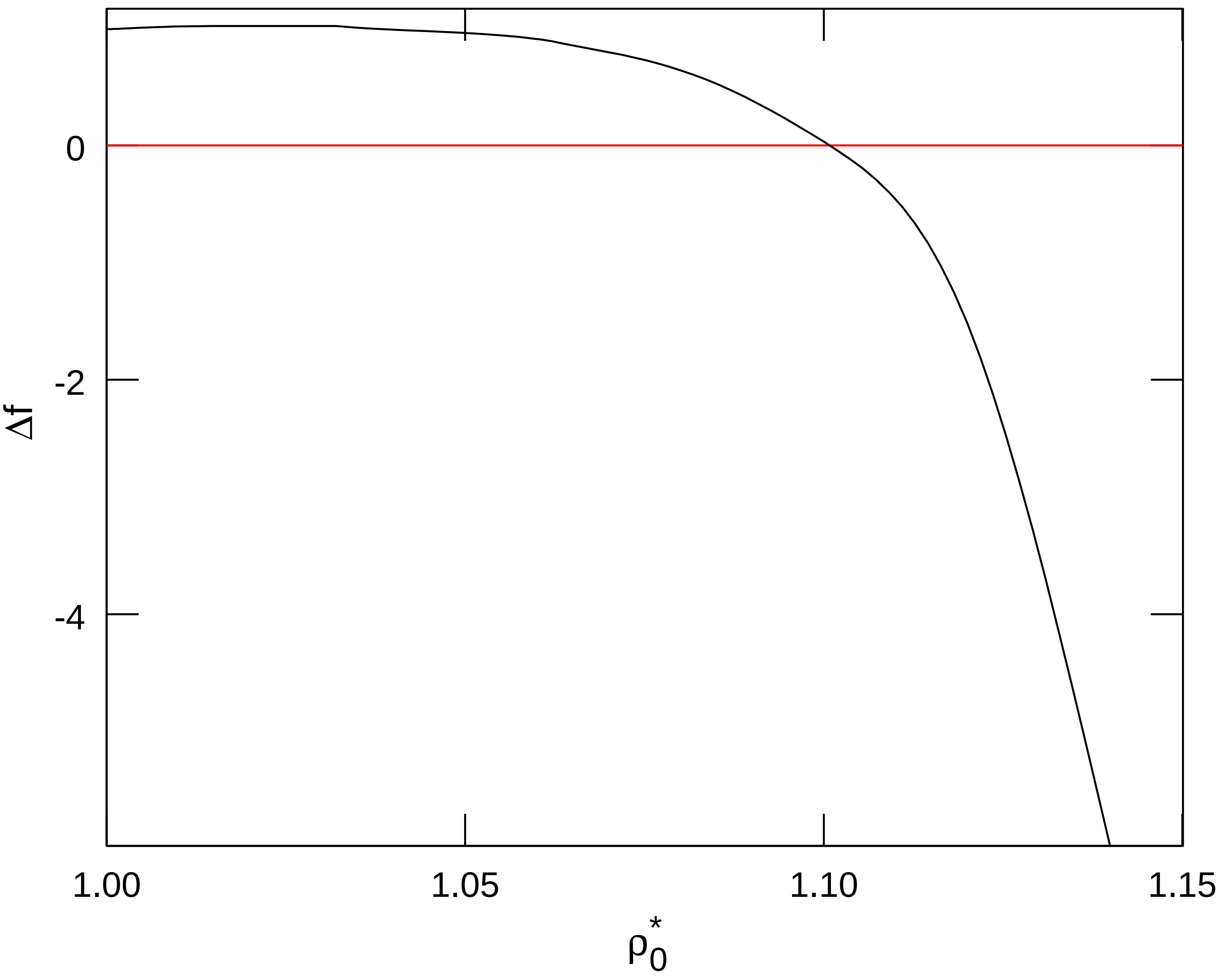

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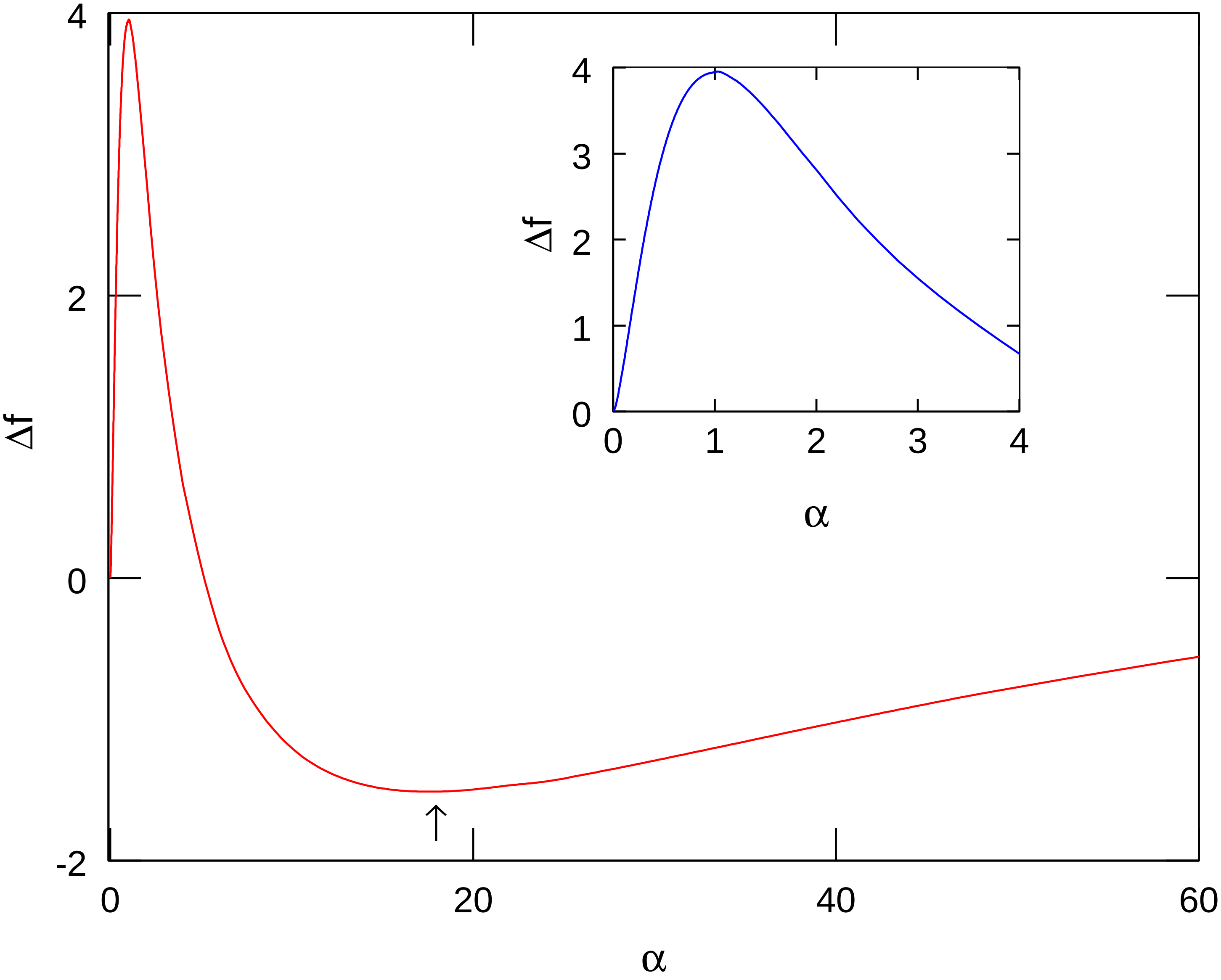

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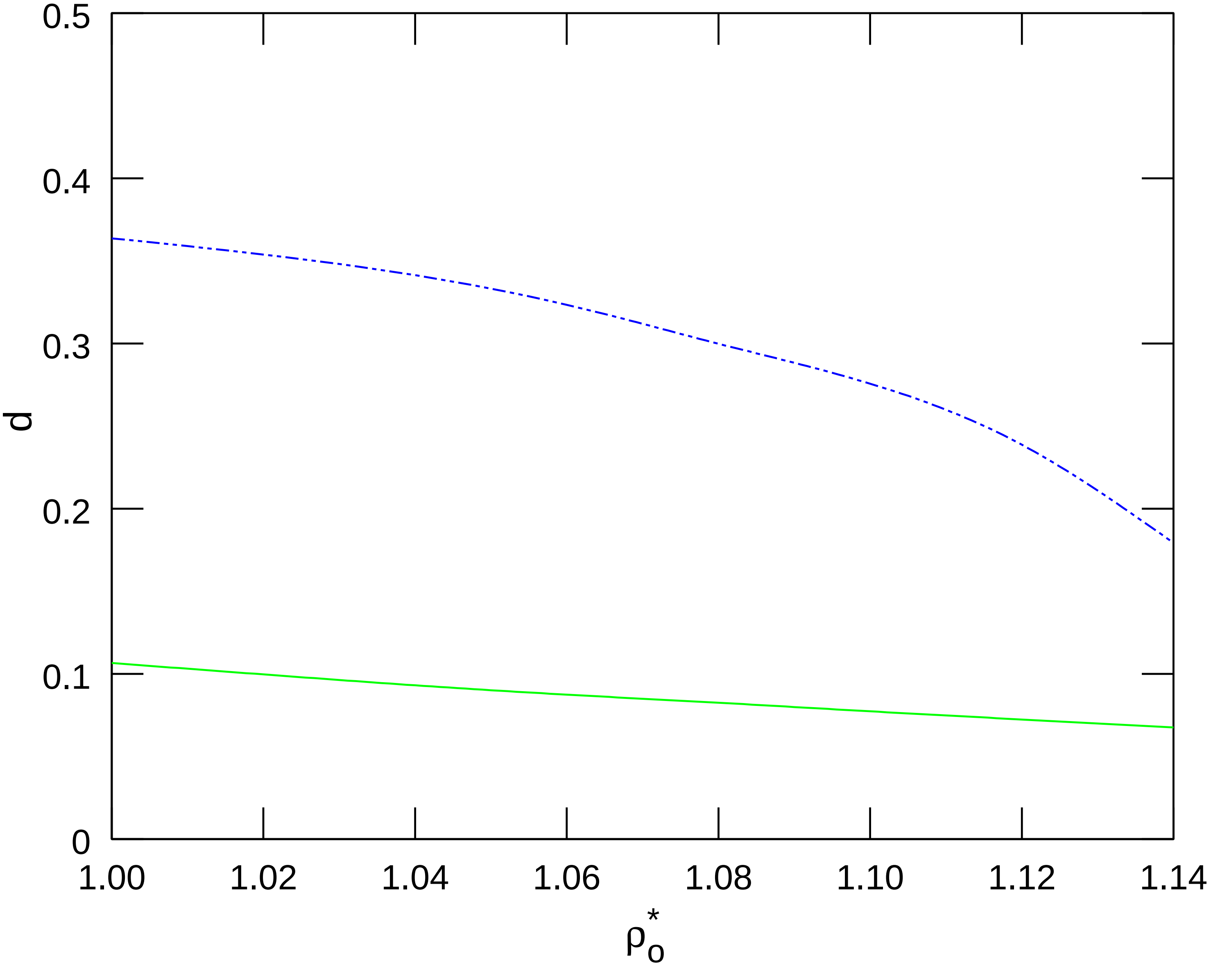
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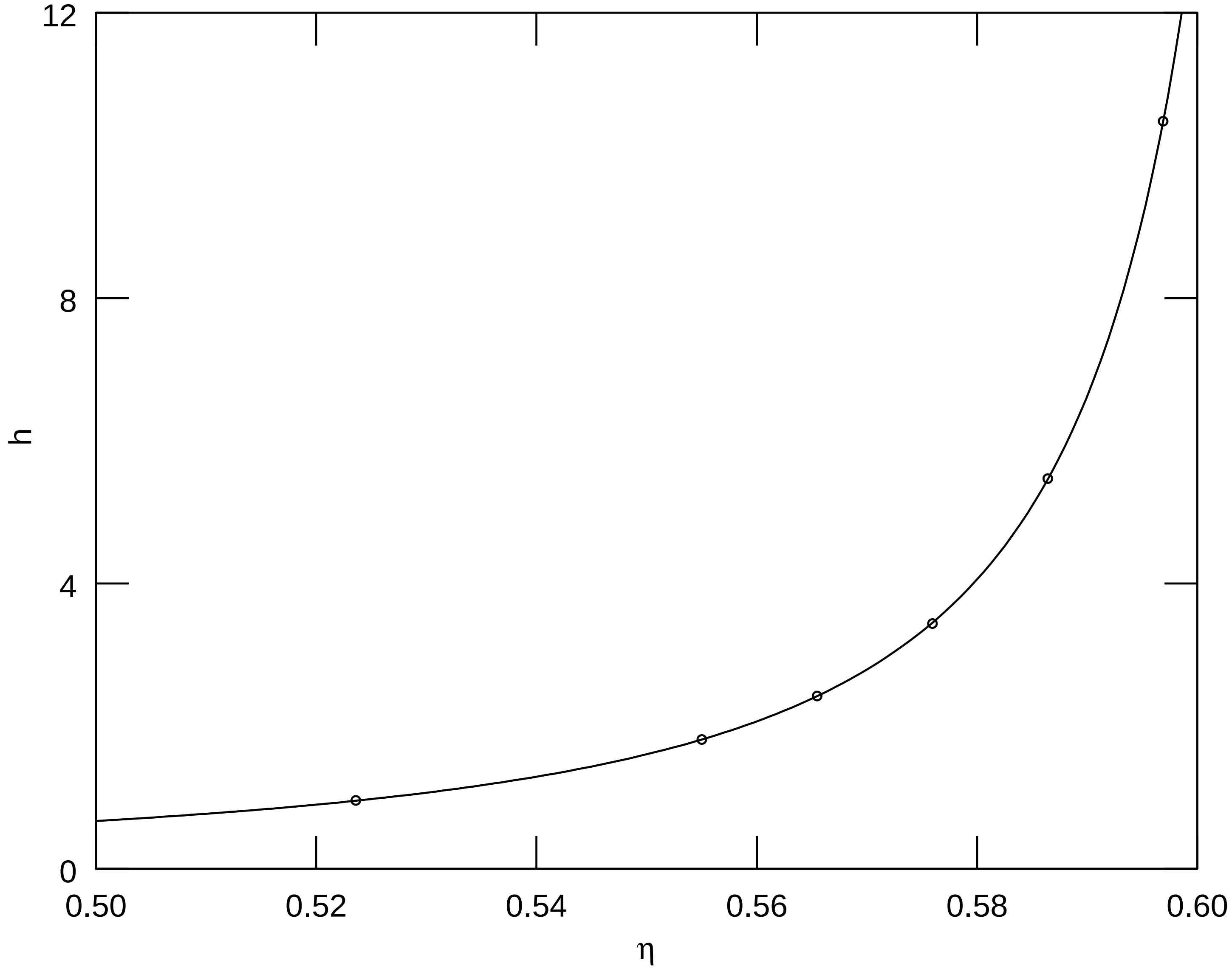
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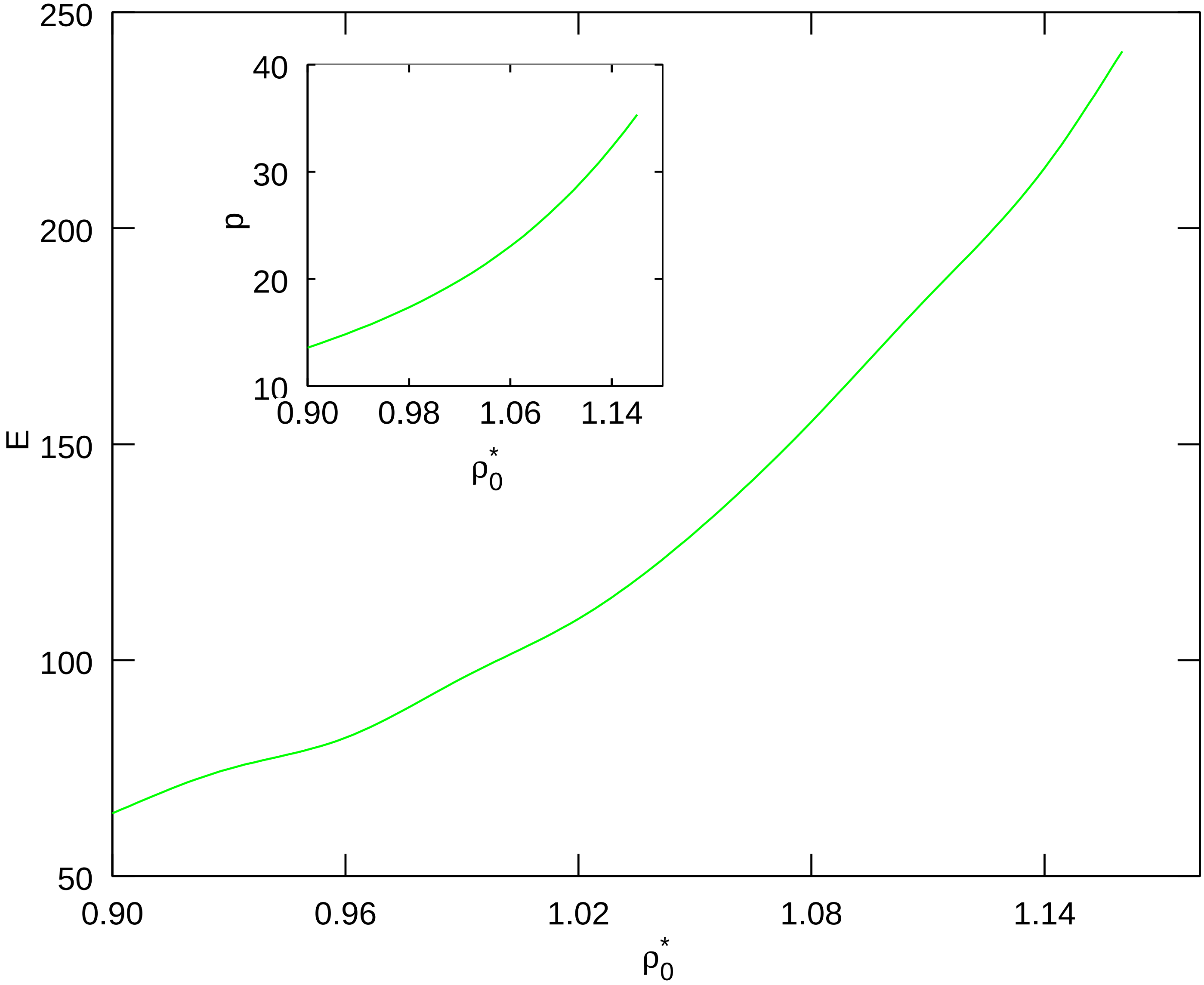

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