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Model for Glass Transition in a Binary fluid from a Mode Coupling approach

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ABSTRACT

We consider the Mode Coupling Theory (MCT) of Glass transition for a Binary fluid. The Equations of Nonlinear Fluctuating Hydrodynamics are obtained with a proper choice of the slow variables corresponding to the conservation laws. The resulting model equations are solved in the long time limit to locate the dynamic transition. The transition point from our model is considerably higher than predicted in existing MCT models for binary systems. This is in agreement with what is seen in Computer Simulation of binary fluids.

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The phenomenon of glass transition has been studied widely in recent years using the mode coupling models for dense liquids. This involves a feed back to the transport properties of the liquid from the coupling of hydrodynamic modes in the liquid. The key aspect of the Mode Coupling Theory [1] (MCT) of Glass transition takes into account the enhanced feed back effects to the viscosity due to the coupling of the slowly decaying density fluctuations. As the density increases beyond a critical value the system undergoes a dynamic transition to a non-ergodic state. The long time limit of the time correlation of density fluctuations is treated as an order parameter for structural relaxation. The transition to the nonergodic state is characterized by a nonzero value of the order parameter or the so-called Non Ergodicity Parameter (NEP). For a binary mixture the self consistent MCT for Glass Transition and the dynamic instability resulting from the feedback mechanism has been studied by several authors [2]-[4] in the past. The model equations in these works predict the dynamic transition at a much lower density compared to the one where a structural arrest is seen in computer simulation of similar systems. This aspect of the Mode coupling model for the binary fluid was indicated in the computer simulations results reported in Ref. [5]. In the present work we have constructed the MCT for the binary system from the equations of the Nonlinear Fluctuating Hydrodynamics(NFH) [6, 7] with proper conservation laws. We consider the correction to the transport coefficient using the mode coupling approximation of dominant density fluctuations. This gives rise to the feed back mechanism on the transport properties. The possible dynamic transition allowed by the model equations is analyzed in terms of the solution of the resulting integral equations. Our main findings are very different from the existing results [3]. The theoretical prediction for the critical density of the dynamic transition now shifts to much higher density bringing it in better quantitative agreement with the computer simulation results.

The slow variables for a binary fluid are partial densities $\rho_s(\vec{x})$, $s = 1, 2$ and total momentum density $\vec{g}(\vec{x})$. These can be defined microscopically as,

$$\begin{aligned} \rho_s(\vec{x}) &= m_s \sum_{\alpha=1}^{N_s} \delta(\vec{x} - \vec{R}^s_\alpha(t)) \\ \vec{g}_i(\vec{x}) &= \sum_{s=1}^{2}\sum_{\alpha=1}^{N_s} \vec{P}^s_{i\alpha}(t)\ \delta(\vec{x} - \vec{R}^s_\alpha(t)) \end{aligned} \tag{1}$$

where $\vec{R}^s_\alpha(t)$ and $\vec{P}^s_{i\alpha}(t)$ are respectively the position and i-th component of the momentum of the α-th particle in the s-th species. N_s is the number of particles in the s-th species in the mixture and the total number of particles is given by, $N = \sum_s N_s$. Generalized Langevin equation for the slow variables are

$$\frac{\partial \rho_s}{\partial t} + \nabla.[\frac{\rho_s}{\rho}\vec{g}] + \ \gamma_{ss\prime}\frac{\delta F_u}{\delta \rho_{s\prime}} = \theta_s \qquad\qquad s = 1, 2 \tag{2}$$

$$\frac{\partial g_i}{\partial t} + \nabla_j \frac{g_i g_j}{\rho} + \rho_s \nabla_i \frac{\delta F_u}{\delta \rho_s} + L_{ij}\frac{\delta F}{\delta g_j} = f_i \tag{3}$$

where the repeated indices are summed over - a convention that we follow in the rest of the paper, unless specifically mentioned. The $\gamma_{s\prime s}$ correspond to the inter and Self-diffusion in the two species. We use the expression [8] $\gamma_{s\prime s} \equiv \partial_i \gamma^{ij}_{s\prime s}\partial_j$. On adding the equations (2) with $s = 1, 2$ for the two components, the continuity equation $\partial\rho/\partial t + \nabla.\vec{g} = 0$ for the total density ρ ($= \rho_1 + \rho_2$) is obtained. Thus the diffusion kernel in the first two equations of (2) for $s = 1, 2$ should cancel. We will use the simple choice here that $\gamma_{21} = -\gamma_{11} \equiv \gamma_o \nabla^2$ and $\gamma_{12} = -\gamma_{22} \equiv \gamma_o\nabla^2$. Similarly the noise corresponding to density fluctuation satisfies $\theta_1 + \theta_2 = 0$. Noise is assumed to be white Gaussian and related to the corresponding bare transport coefficients. The f and θ are taken to be uncorrelated. The bare transport coefficient L_{ij} can be expressed in terms of the shear and bulk viscosities η_o and ζ_o in an isotropic fluid. The longitudinal viscosity is given by $\Gamma_o = (4\eta_o/3 + \zeta_o)/\rho_o$.

The Free energy functional F that is used in constructing the equations of the Nonlinear Fluctuating Hydrodynamics plays an important role here. It has two parts, the kinetic and the "potential" respectively denoted by F_k and F_u. In computing the kinetic energy contribution, we follow the standard procedure due to Langer and Turski [9].

$$F_k = \frac{1}{2}\int d\vec{x}[g^2(\vec{x})/\rho(\vec{x})] \tag{4}$$

where the total density $\rho = \rho_1 + \rho_2$ appears in the denominator of (4). For the potential part of the free energy there is an ideal gas contribution together with the interaction term. We use the standard form [10, 8] in terms of the direct correlation functions [10],

$$F_u(\rho) = \frac{1}{m_s}\int d\vec{x}\rho_s(\vec{x})\ [\ln\frac{\rho_s(\vec{x})}{\rho_{os}} - 1] - \frac{1}{2m_s m_{s\prime}}\int d\vec{x}d\vec{x}\prime c_{ss\prime}(\vec{x} - \vec{x}\prime)\delta\rho_s(\vec{x})\delta\rho_{s\prime}(\vec{x}\prime) \tag{5}$$

From the dynamic equations (2) and (3), we compute the time correlation function [11] $C_{ss\prime}(\vec{x} - \vec{x}\prime, t - t') = \frac{1}{N} < \psi_s(\vec{x}, t)\psi_{s\prime}(\vec{x}\prime, t\prime) >$ between the hydrodynamic variables ψ_s and $\psi_{s\prime}$. The normalized form of the density-density correlation functions, $R_{ss\prime}(q, z)$, is defined as $R_{ss\prime}(q, z) = C_{ss\prime}(q, z)/\sqrt{\chi_{ss}\chi_{s\prime s\prime}}$ where $\chi_{ss\prime}$ is the equal time density correlation function between i-th and j-th species. The partial structure factor $S_{ss'}$ [12] is defined from the $\chi_{ss'}$ through the relation $\chi_{ss'} = a_s a_{s\prime} S_{ss\prime}$ where $a_s = m_s\sqrt{n_s}$, m_s and n_s are respectively mass and particle density corresponding to the s-th species. We compute the mode coupling contribution to the transport coefficients by treating the non linearities in equations of motion with standard methods [11]. The renormalized form for the longitudinal viscosity at the one loop order is given by,

$$\Gamma(q, t) = \frac{1}{2\rho_0 q^2}\int \frac{d\vec{k}}{(2\pi)^3} V_{ss\prime}(q, k)\ V_{ll\prime}(q, k_1)\ C_{l\prime s\prime}(k, t)\ C_{ls}(k_1, t), \tag{6}$$

where $k_1 = q - k$. The vertex function $V_{ss\prime}(q, k)$ is given by,

$$[m_s m_{s\prime}]V_{ss\prime}(q, k) = (\hat{q}.k)\ \ \tilde{c}_{ss\prime}(k) + \hat{q}.k_1\ \ \tilde{c}_{ss\prime}(k_1) \tag{7}$$

with $c_{ss\prime}(\vec{x} - \vec{x}\prime)$ denoting the equilibrium two particle direct correlation function [13]. The quantity $\tilde{c}_{ss\prime}(q) = (n_s n_{s\prime})^{\frac{1}{2}} c_{ss\prime}(q)$ is related to the structure factor $S_{ss\prime}(q)$ through the Ornstein Zernike relation $[\delta_{ls} - \tilde{c}_{ls}(q)]S_{ls\prime}(q) = \delta_{ss\prime}$. In obtaining the above expression(6) we have considered only the coupling of the density fluctuations coming from the non linearity in the Pressure term that appears in the momentum conservation equation (3). This involve taking the density fluctuations as dominant and using the one loop correction or the so-called Kawasaki approximation to the four point functions to the transport coefficients. This is done in the same spirit of the self-consistent mode coupling approximation of taking density fluctuations to be dominant as in the case of one component fluid. We like to point out here that in the appropriate limit these results reduce to the one component fluid result that *is in complete agreement* with all other wave vector dependent models [14] for one component systems.

Next we consider the implications on the dynamic transition as a result of the new set of integral equations for the NEP. The ideal glass phase is characterized by the nonergodicity parameter, $\lim_{t\to\infty} R_{ss'}(q,t) = f_{ss'}(q)$. The correlation of density fluctuations is expressed in terms of the renormalized transport coefficients [7]. In the asymptotic limit of long times we obtain the following set of self-consistent equations for the NEP's $f_{ss'}(q)$,

$$f_{ss'}(q) = \frac{\Im_{ss'}(q)\Gamma(q)}{1+\Omega(q)\Gamma(q)} \quad . \tag{8}$$

Here $\Gamma(q)$ is the long time limit of $\Gamma(q,t)$ given by equation (6). $\Omega(q)$ and $\Im(q)$ are given by,

$$\Omega(q) = \Delta_{ss'}S_{ss'}(q) \qquad \Im_{ss'}(q) = \frac{\Delta_{ij}S_{is}(q)S_{js'}(q)}{[S_{ss}(q)S_{s's'}(q)]^{\frac{1}{2}}} \tag{9}$$

with $\Delta_{ss'} = a_s a_{s'}/\rho_o$. Eq. (8) constitute a set of coupled nonlinear integral equations for the non-ergodicity parameters $f_{ss'}$. The dynamic instability of the ideal glass transition in the binary system is then located from the *self-consistent* solution of eq. (8) by iterative method in a similar manner as in the one component systems. The static structure factor goes as an input in the calculation. The interaction potential for the system enters the present theoretical description for the dynamics through this thermodynamic quantity. Due to the available simple formulation for the structure and in order to keep continuity with pervious works on binary fluids [3] we will choose a mixture of hard spheres. This is described by three independent parameters, (a) The fractional concentration of particles $x_s(= N_s/N)$, (b)

The size ratio $\alpha (= \sigma_1/\sigma_2)$, and (c) The total packing fraction $\eta = \eta_1 + \eta_2$ where η_1 and η_2 are the packing fractions of the individual species. $\eta_s = \frac{\pi}{6} n_s {\sigma_s}^3$, n_s and σ_s being respectively the number of particles per unit volume and diameter of the s-th species (s =1,2). We choose σ_2, diameter of bigger species, as the unit of length. The structure factors for the binary liquid required in computing the mode coupling vertex functions appearing in (8) are obtained using the standard results of the solution of Percus Yevick equations for the hard sphere [15, 12] mixture. We solve for the nonlinear integral equations to search the nontrivial fixed points with non zero values of $f_{ss'}(q)$. Depending on the thermodynamic parameters described above a nonergodic phase is seen beyond a critical density. The results remain unchanged if we replace x and α respectively by $1 - x$ and $1/\alpha$ meaning an interchange of the label for the two species. In Fig. 1, we show the non-zero solutions for the NEPs f_{11} and f_{22} respectively for the critical packing fraction $\eta_c = .59$. The nature of the ideal glass instability in the binary mixture is dependent on the size ratio α as well as the relative abundance x. We list below a few comments.

(i) The NEP f_{22} reach a small value at an intermediate wave number q_m depending on x (fraction of the bigger particles 2). As the relative proportion x is increased this wave number q_m become 0, beyond a value $x \geq x_0$. This behavior is primarily due to the nature of the structure function $\Im_{ss'}(q)$ that appears in the mode coupling equation (8) for the NEPs. In the inset of Fig. 1, we show how the position of q_m^* shifts with x at $\alpha = .7$ and becomes zero at $x_0 = .977$.

(ii) The transition to the non-ergodic phase, indicating a structural arrest, shifts to higher densities as the size ratio (α) is decreased. For example, at $x = .1$ and $\alpha = .2$ *structural arrests are absent* up to very high densities ($\eta \leq .64$). This absence of transition here can be explained from the fact that for low values of x and size ratio α the smaller particles can diffuse easily through the cage of the bigger particles and hence the structural arrest is avoided. Indeed it is a competition between the two quantities, the size ratio α allowing easier movement of the particles and x giving the relative abundance of the voids formed between bigger particles. To stress the importance of the present work, it should be noted that, with the same values of the thermodynamic parameters the Ref. [3] report a transition in the range $(.51 \leq \eta_c \leq .52)$.

(iii) With the ratio of particle sizes, α smaller than .75, there is no structural arrest, over a range $(.22 \leq x \leq .58)$. In the earlier mode coupling model equations [3] this sensitivity to the sizes of the particles (α) and (x) was absent. The same qualitative dependence of α on the freezing in a binary fluid system has also been reported in studies related to the thermodynamics [16] of the system.

Fig. 2 shows the critical packing fraction (η_c) with x at constant $\alpha = 0.8$. If the particles are similar to each other $(\alpha = 1)$ and x close to unity, the dynamic instability occurs at $\eta = 0.515$ that is very close to the critical packing fraction (with the use of Percus-Yevick Structure factor) for a single component system as is expected to be the case.

As a result of the mode coupling instability, the transverse current correlation function [8] also develops propagating shear modes [17]. The expression for the speed of the shear waves (c_T) in the binary fluid can be obtained in terms of nonergodicity parameters in the following form,

$$c_T{}^2 = \frac{1}{60\pi^2}\sqrt{\frac{x_1 x_2}{n_1 n_2}} \int dk k^4 \tilde{c\prime}_{ll\prime}(k) \tilde{c\prime}_{ss\prime}(k) f_{s\prime l\prime}(k) f_{sl}(k) \sqrt{S_{ss}(k) S_{ll}(k) S_{s\prime s\prime}(k) S_{l\prime l\prime}(k)} \qquad (10)$$

where $\tilde{c\prime}_{ss\prime}(q)$ denotes derivative of $\tilde{c}_{ss\prime}(q)$ with respect to q. In Fig. 3, we show the behavior of c_T with (x) for two different size ratios(α).

In the present work we have obtained, from the equations of Nonlinear fluctuating hydrodynamics, the feedback mechanism of the self consistent MCT. Solutions of our model equations indicate that the dynamic instability *shifts to much higher densities* than what is predicted in the earlier works [3]. This also agrees with the trend seen in computer simulation results[5]. The kinetic energy term, eq. (4), of the Free energy functional that is used here is crucial for the construction of the model equations. This is also essential for obtaining in the momentum conservation equation the convective or the so-called Navier-Stokes term reflecting Galilean invariance. In considering the dynamic nonlinearities that gives rise to the mode coupling instability we have taken here a driving Free energy functional of Gaussian form. Thus origin of the nonlinearity is dynamic as is the case for the one component fluid. The higher order terms in the Free energy functional will give rise to nonlinearities in the density equations and this will require for the renormalization of the diffusion coefficients (γ_o). The lowest order vertex then is proportional to the γ_o and will come from non-Gaussian terms in the free energy functional involving higher order direct correlation functions. We end the paper with few comments,

(i) The earlier versions of the MCT [3] for binary systems can be reproduced from our work, using the *same Gaussian Free Energy functional* $F_u$as considered here, if one (a) replaces the kinetic energy term with [8] $F_k = \int d\vec{x}[g_1^2/2\rho_1 + g_2^2/2\rho_2]$, $\vec{g_1}$ and $\vec{g_2}$ denoting the momentum densities of the individual components in the binary system, both treated as two *separately* conserved variables and (b) ignore the inter diffusion γ as well. (a) will also violate the Galilean invariance in the hydrodynamic equations.

(ii) Here we have considered the dynamics of density correlation functions only in the asymptotic limit so as to study the implications on the dynamic transition. The utility of the present approach is demonstrated through the better result for the location of the dynamic transition. To study the dynamics over different time scales the time dependent mode coupling equations for the various density correlation functions has to be considered. These equations involve the bare transport coefficients γ_{ij} and L and will be reported elsewhere [18].

(iii) Finally, the complete picture of the dynamics will involve computing the coupling to the current correlations [7] that restores the ergodicity in the longest time scale [18].

The present work treats the dynamics for the two component system with the correct set of slow variables and shows quantitative agreement of MCT results with computer simulation studies and remedies the theories presented in earlier works.

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Figure Captions

Fig. 1 : nonergodicity parameters $f_{11}(q^*)$(solid line) and $f_{22}(q^*)$ (broken line) at $\eta_c = .59$, x=.8 and $\alpha = .7$. q^*=qσ_2 is plotted along x axis. Inset shows q^*_m(see text) Vs x plot for $\alpha = .8$ and $\eta = .59$

Fig. 2 : critical value of η_c is plotted with x for $\alpha = 0.8$. Regions "a" and "b" represent liquid and glass phases respectively.

Fig. 3 : speed of shear mode c_T is plotted as a function of x for two values of α=0.85 (solid) and 0.90 (broken) at $\eta = .57$.

References

[1] B. Kim and G. F. Mazenko, Adv. Chem. Phys. **78**, 129 (1990).

[2] U. Krieger and J. Bosse, Phys. Rev. Lett. **59** 1601 (1987); J. Bosse and J. S. Thakur, Phys. Rev. Lett. **59** (9),998 (1987).

[3] J. S. Thakur and J. Bosse, Phys. Rev. A **43**, 4378 (1991); Phys. Rev. A **43** 4388 (1991); J. Bosse, Z. Phys. B 103, 357-362 (1997).

[4] M. Fuchs and A. Latz, Physica A **201** (1993) 1-13.

[5] Markus Nauroth and Walter Kob, Phys. Rev. E **55**, 657 (1996).

[6] T. R. Kirkpatrick and J. C. Neiuwoudt, Phys. Rev. A **33** 2658 (1986).

[7] Shankar P. Das and Gene F. Mazenko, Phys. Rev.A **34**,2265 (1986).

[8] Supurna Sinha and M. Cristina Marchetti, Phys. Rev. A **46** 4942 (1992).

[9] J. S. Langer and L. A. Tursky, Phys. Rev. A **8**,3230 (1973).

[10] T. V. Ramakrishnan and M. Yussouff, Phys. Rev. B **19** 2775 (1979).

[11] Gene F. Mazenko,Sriram Ramaswamy and John Toner, Phys. Rev. A **28**,1618 (1983).

[12] N. W. Ashcroft and David C. Langreth, Phys. Rev. **156**, 685 (1967).

[13] J. P. Hansen and J. R. McDonald, I. *Theory of Simple Liquids*, (Academic, London, 1976).

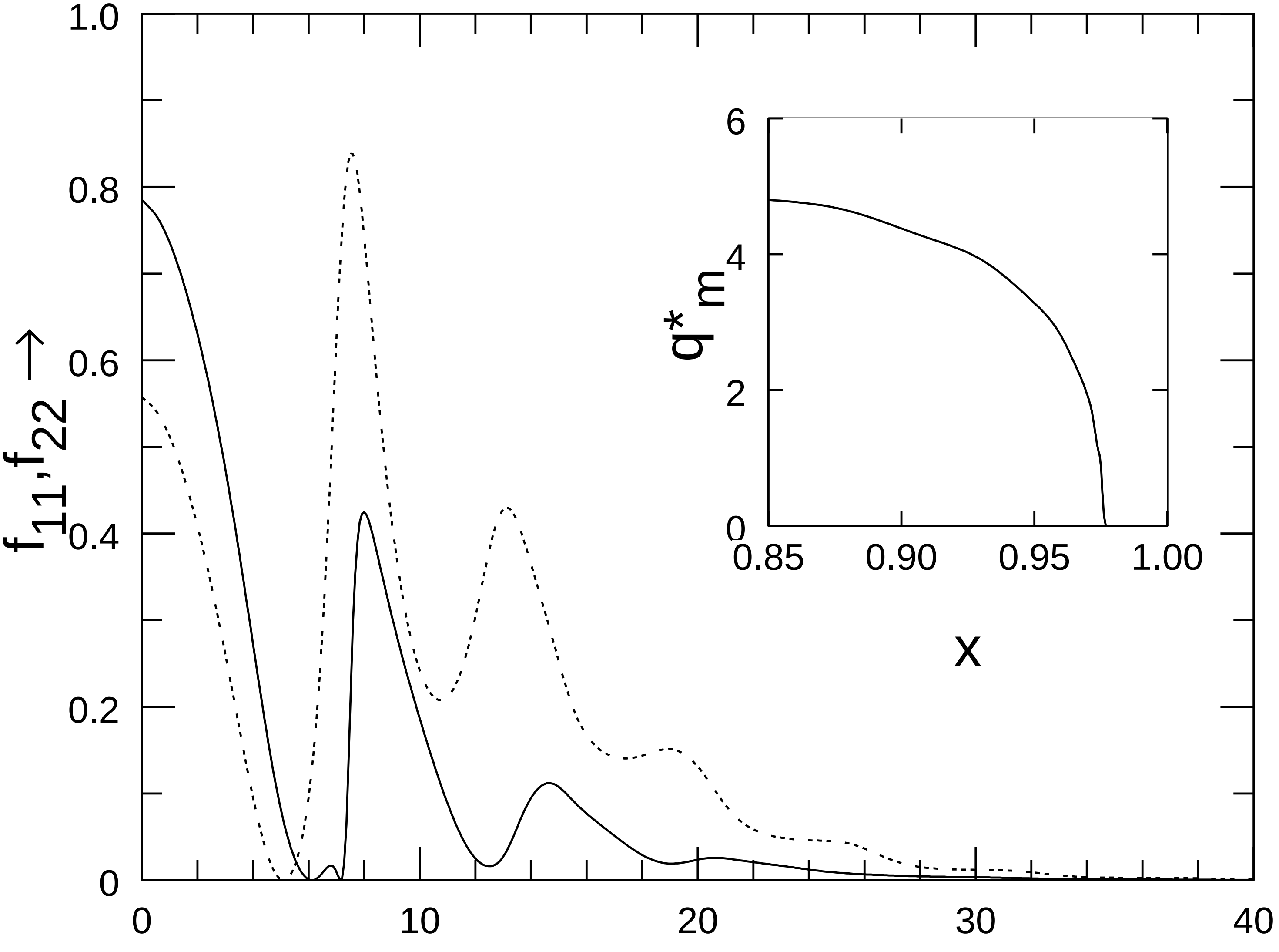
[14] U Bengtzelius, W. Gőtze and A. Sjőlander, J.Phys.C Solid State Phys. **17** (1984) 5915-5934.

[15] J. L. Lebowitz, Phys.Rev. **133** A895 (1964).

[16] J. L. Barrat, M. Baus, J. P. Hansen, J. Phys. C **20**, 1413 (1987).

[17] Rajeev Ahluwalia and Shankar P. Das, Phys. Rev. E **57**, 5771 (1998)

[18] Upendra Harbola and Shankar P. Das, To be published



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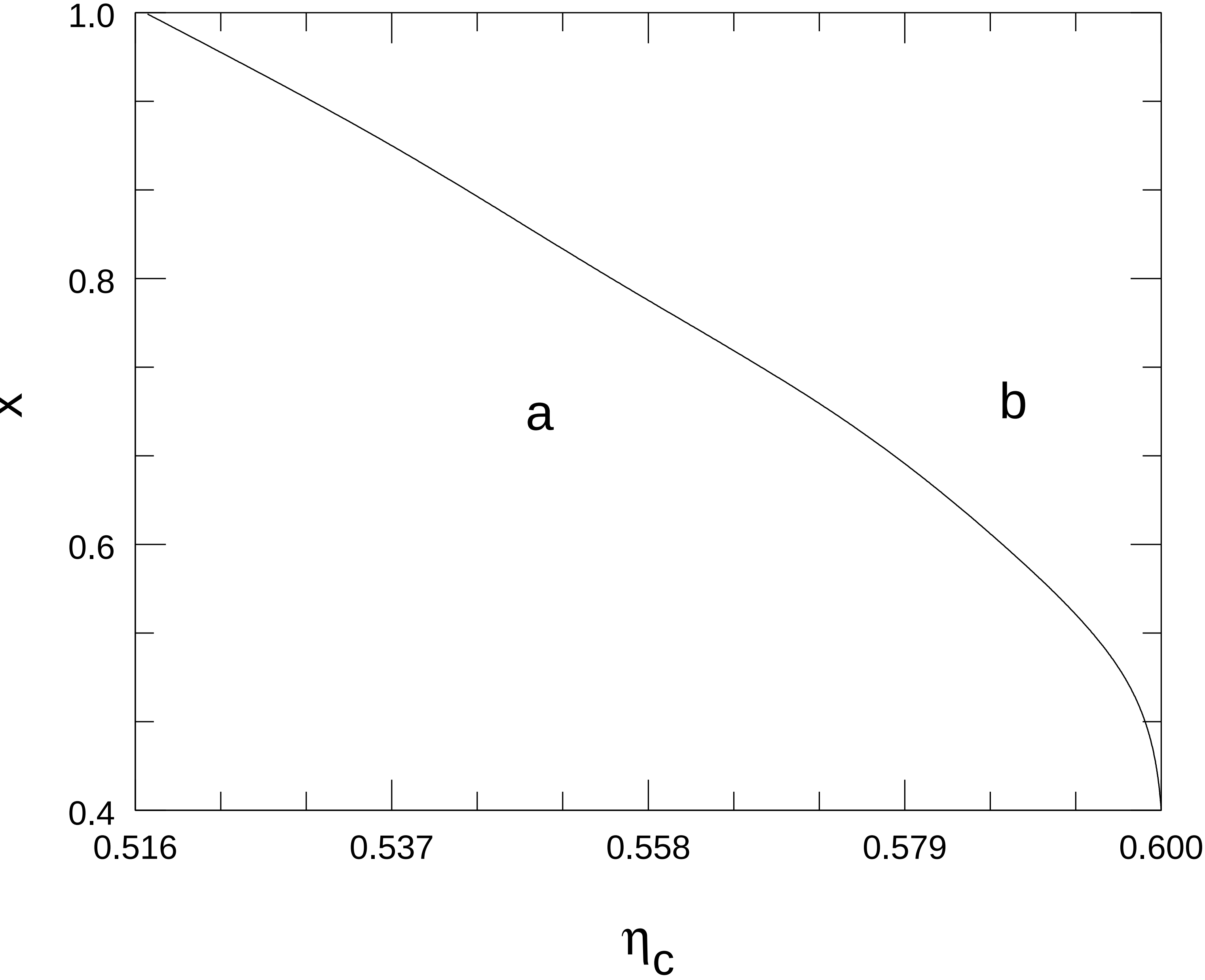
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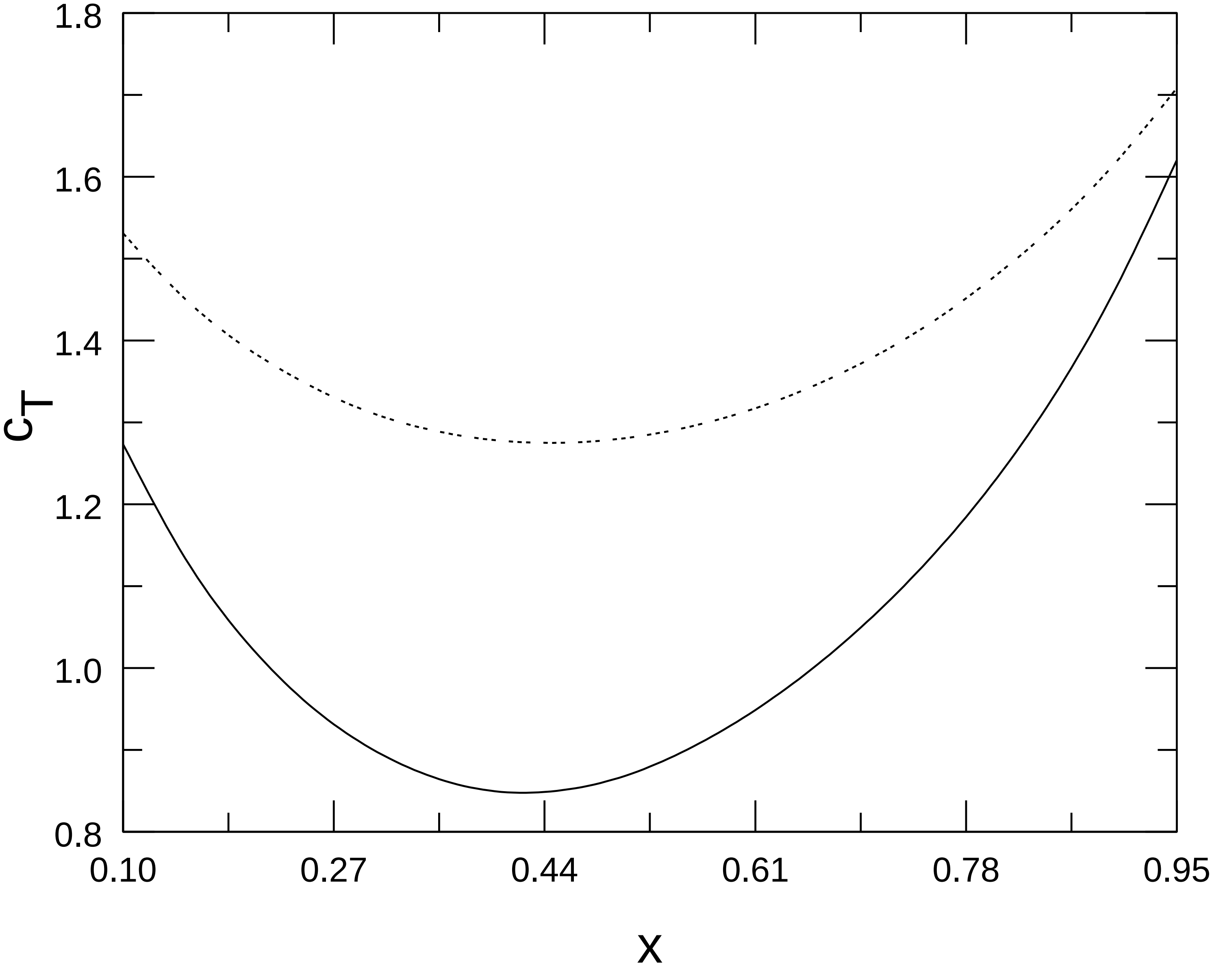
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