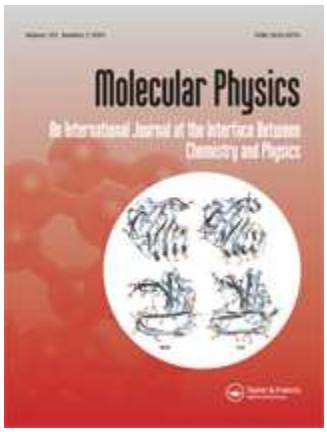
Pertubation Theory for Systems With Strong Short-Ranged Interactions

Per Sillrén, Jean-Pierre Hansen



Pertubation Theory for Systems With Strong Short-Ranged Interactions

Journal:	*Molecular Physics*
Manuscript ID:	TMPH-2007-0082.R1
Manuscript Type:	Full Paper
Date Submitted by the Author:	17-Apr-2007
Complete List of Authors:	Sillrén, Per; Chalmers University of Technology, Applied Physics Hansen, Jean-Pierre; University of Cambridge, Chemistry
Keywords:	Perturbation Theory, Hard Sphere, Liquid Mixture, Strong Interaction, Phase separation
Note: The following files were submitted by the author for peer review, but cannot be converted to PDF. You must view these files (e.g. movies) online.	
Paper.tex ._Paper.tex	

Pertubation Theory for Systems With Strong Short-Ranged Interactions

PER SILLRÉN * and JEAN-PIERRE HANSEN †

Department of Chemistry, University of Cambridge,

Lensfield Road, Cambridge CB2 1EW, UK

April 23, 2007

Abstract

We propose a variant of thermodynamic perturbation theory based on the Mayer f-function which is applicable to strongly repulsive, and even singular interactions. The expansion of the free energy is successfully tested against known "exact results" for hard sphere fluids, and then applied to binary mixtures of particles with non-additive hard cores or shouldered potentials. The resulting phase diagrams agree well with existing simulation data and theoretical predictions.

*Present address: Department of Applied Physics, Chalmers University of Technology, SE-412 96 Göteborg, Sweden

†Corresponding Author: jph32@cam.ac.uk

1 Introduction

Thermodynamic Perturbation Theory of fluids goes back to van der Waals [1], and was cast in modern Statistical Mechanics language by Zwanzig [2]. It is based on the idea that the molecular structure of dense fluids and solids is essentially determined by the short-range repulsive interactions between atoms or molecules (exluded volume effect), and that smoothly varying long-range attractions between molecules, essential for cohesion, can be considered as a perturbation to the reference system of particles interacting solely through the steep repulsive forces. This perturbation approach was applied with considerable success to simple liquids, culminating in the theories of Barker and Henderson [3], and of Andersen, Chandler, and Weeks [4]. The success of these theories relies on the assumption that excluded volume effects prevent strong local fluctuations, and that the contribution $w(r)$ to the full inter-atomic potential, treated as a perturbation, varies slowly in space and is comparable to k_BT or less. Zwanzig's version of thermodynamic perturbation theory is well adapted to that case, but is expected to fail when the perturbation $w(r)$ is strongly repulsive and rapidly varying or singular.

In this paper we present a modified version of thermodynamic perturbation theory which is capable of dealing with strongly repulsive perturbations and non-additivity of hard core interactions. It shifts the focus of the perturbation expansion from the perturbation potential $w(r)$ to the corresponding Mayer f-function f(r), which remains a finite function of r for any repulsive interaction. The present approach buids on and extends earlier work by Kincaid et al. [5] (who considered only the first order term in the f-function expansion) and by Pelissetto and Hansen [6]. **The formal expressions for the free energy obtained in Sections 2**

and 3 below are reminiscent of those derived by Barker and co-workers [7, 8, 9] via a cluster expansion route, and used by those authors to express the free energy of a fluid mixture in terms of that of a one-component reference fluid, in the spirit of Longuet - Higgins' conformal solution theory [10].

The present theory is of relevance to a number of physical situations. One example concerns a number of metals, like Cs and Ce, which undergo electronic "collapse" under pressure. This physical situation may be modelled by a repulsive shouldered potential [11], which leads to an isostructural solid-solid transition [5, 12, 13] and to a melting curve maximum [14].

The second example is that of multi component colloidal dispersions, where non-additive hard core interactions are the rule rather than the exception [15]. An extreme case of non-additivity is provided by the Asakura-Oosawa model of colloid-polymer mixtures [16]. Examples of such systems will be considered as applications of the f-function perturbation theory later in this paper.

2 Mayer Function Perturbation Theory

The basics of thermodynamic perturbation theory are well documented [2, 3, 17], and are only briefly summarised here for a one component system. Consider a system of N particles whose total interaction energy is split into two parts

$$V_\lambda(\mathbf{r}^N) = V_0(\mathbf{r}^N) + W_\lambda(\mathbf{r}^N), \tag{1}$$

where V_0 corresponds to a reference system while the perturbation is gradually switched on by varying the coupling constant from λ_0 (such that $W_{\lambda_0} = 0$) to λ_1

leading back to the full interaction term of the system of interest. If $Z_N(\lambda)$ denotes the classical configuration integral for a given value λ of the coupling constant, then the derivative of the excess (non-ideal) part of the Helmholtz free energy is given by

$$\beta\frac{\partial F^{ex}(\lambda)}{\partial\lambda} = \frac{1}{Z_N(\lambda)}\int \beta\frac{\partial W_\lambda}{\partial\lambda}e^{-\beta V_\lambda}d\mathbf{r}^N = \langle\beta W'_\lambda\rangle_\lambda, \tag{2}$$

where $\beta = 1/k_BT$, the prime denotes a derivative with respect to λ, and $\langle\cdot\rangle_\lambda$ denotes a statistical average over a canonical ensemble with Boltzmann weight $e^{-\beta V_\lambda}$. A Taylor expansion of the r.h.s. of eq. (2) in powers of $\Delta\lambda = \lambda_1 - \lambda_0$, followed by integration of both sides over $\lambda \in [\lambda_0, \lambda_1]$ leads to the standard result [2, 17]

$$\begin{aligned}
\beta F^{ex}(\lambda_1) &= \beta F^{ex}(\lambda_0) + \left\langle\beta W'_{\lambda_0}\right\rangle_{\lambda_0} + \\
&+ \frac{1}{2!}\langle\beta W''_{\lambda_0}\rangle_{\lambda_0} - \frac{1}{2!}\left\langle\left(\beta W'_{\lambda_0} - \left\langle\beta W'_{\lambda_0}\right\rangle_{\lambda_0}\right)^2\right\rangle_{\lambda_0} + \\
&+ \frac{1}{3!}\langle\beta W'''_{\lambda_0}\rangle_{\lambda_0} + \frac{3}{3!}\left(\langle\beta W'_{\lambda_0}\beta W''_{\lambda_0}\rangle_{\lambda_0} - \langle\beta W'_{\lambda_0}\rangle_{\lambda_0}\langle\beta W''_{\lambda_0}\rangle_{\lambda_0}\right) + \\
&+ \frac{1}{3!}\left\langle\left(\beta W'_{\lambda_0} - \langle\beta W'_{\lambda_0}\rangle_{\lambda_0}\right)^3\right\rangle_{\lambda_0} + \cdots
\end{aligned} \tag{3}$$

where we set $\lambda_0 = 0$ and $\lambda_1 = 1$.

In the most common version of perturbation theory, one chooses

$$W_\lambda(\mathbf{r}^N) = \lambda W(\mathbf{r}^N), \qquad \lambda \in [0, 1]. \tag{4}$$

With this linear choice, adopted by Zwanzig [2], all derivatives of W_λ beyond the first vanish, so that the second and higher order terms in the expansion in eq. (3) simplify [17].

We shall henceforth make the usual assumption that W is pairwise additive,

i.e.

$$W(\mathbf{r}^N) = \sum_{i=1}^{N} \sum_{j>i}^{N} w(\mathbf{r}_i, \mathbf{r}_j). \tag{5}$$

Zwanzig's series may then be formally regarded as a cumulant expansion in "powers" of βw, which is not expected to converge when $|\beta w| >> 1$, and which is meaningless if w is singular as is the case for hard-core interactions. To cope with such situations, it is natural to focus on the Mayer f-function associated with the perturbation potential w:

$$f(\mathbf{r}_i, \mathbf{r}_j) = e^{-\beta w(\mathbf{r}_i, \mathbf{r}_j)} - 1 \tag{6}$$

as one does in the derivation of the virial expansion of the equation-of-state or the free energy around a non-interacting reference system [17]. A natural choice for βW_λ is hence [6]

$$\beta W_\lambda(\mathbf{r}^N) = -\sum_{i=1}^{N} \sum_{j>i}^{N} \ln(1 + \lambda f(\mathbf{r}_i, \mathbf{r}_j)), \qquad \lambda \in [0, 1]. \tag{7}$$

The derivatives with respect to λ taken at $\lambda = 0$, are easily calculated to be

$$\begin{aligned}
\beta W' &= -\sum_{i=1}^{N} \sum_{j>i}^{N} f(\mathbf{r}_i, \mathbf{r}_j) \\
\beta W'' &= \sum_{i=1}^{N} \sum_{j>i}^{N} f^2(\mathbf{r}_i, \mathbf{r}_j) \\
\beta W''' &= -2! \sum_{i=1}^{N} \sum_{j>i}^{N} f^3(\mathbf{r}_i, \mathbf{r}_j) \\
&\vdots \\
\beta W^{(n)} &= (-1)^n (n-1)! \sum_{i=1}^{N} \sum_{j>i}^{N} f^n(\mathbf{r}_i, \mathbf{r}_j).
\end{aligned} \tag{8}$$

These may now be substituted into eq. (3) to yield

$$\beta F_1^{ex} = -2\pi N\rho \int_0^\infty g_0^{(2)}(r) f(r) r^2 dr \tag{9}$$

where we have assumed that the pair interaction is spherically symmetric, i.e. depends only on $r = |\mathbf{r}_i - \mathbf{r}_j|$, $g_0^{(2)}(r)$ is the pair distribution function of the reference system, and $\rho = N/V$ is the number density. The second order term reads

$$\beta F_2^{ex} = \pi N\rho \int_0^\infty g_0^{(2)}(r) f(r)^2 r^2 dr - \frac{1}{2}\left\langle \left(\beta W' - \langle \beta W' \rangle\right)^2 \right\rangle_0, \tag{10}$$

where the fluctuation term can be expanded in terms of the pair, triplet and quadruplet distribution functions of the reference system [2, 3, 17]; it has exactly the same structure as the second order term in the Zwanzig perturbation theory, with the perturbation potential βw replaced by the Mayer f-function, eq. (6). In the applications we have not attempted to evaluate this fluctuation term because the higher order distribution functions are generally unknown, and must be approximated. Instead, we have used Barker and Henderson's "local compressibility" approximation [3], according to which

$$\frac{\beta^2}{2}\left(\left\langle (W')^2 \right\rangle_0 - \langle W' \rangle_0^2\right) = \frac{\pi\rho}{\frac{\partial(\beta P_0)}{\partial\rho}} \frac{\partial}{\partial\rho}\left(\rho \int_0^\infty f(r)^2 g(r) r^2 dr\right), \tag{11}$$

where P_0 is the pressure of the reference system.

Higher order terms in the series (3) become increasingly complicated except in the specific case considered in [6], where the third order term is tractable, as will be shown in the next section.

In the limiting case where the reference system is an ideal gas of non-interacting

particles, i.e. $V_0(\mathbf{r}^N) \equiv 0$ the first order correction (9) (with $g_0^{(2)}(r) = 1$ over the interval of interest) reduces to the familiar second virial coefficient correction to the ideal gas free energy. In the same limit $\beta F_2^{ex} = 0$.

3 Generalisation to Binary Mixtures

The Mayer function perturbation expansion derived in the previous section for a one-component system is easily extended to multi-component systems with the concomitant complication linked to summations over pairs of species. Since non-additive interactions in binary AB mixtures, whereby essentially

$$\sigma_{AB} \neq \frac{\sigma_A + \sigma_B}{2}, \tag{12}$$

are particularly relevant for binary colloidal systems or colloid-polymer mixtures, we restrict the subsequent case to such mixtures, treating the deviation from additivity as the perturbation $w_{AB}(r)$. In other words

$$W(\mathbf{r}^N) = W_{AB}(\mathbf{r}^N) = \sum_{i=1}^{N_A} \sum_{i>j}^{N_B} w_{AB}(\mathbf{r}_i, \mathbf{r}_j) \tag{13}$$

where N_A and N_B are the numbers of particles of both species and $N = N_A + N_B$ is the total number of particles. We will also use the molar fractions $x_A = N_A/N$ and $x_B = 1 - N_A$. Making once more the choice

$$\beta W_{AB,\lambda}(\mathbf{r}^N) = -\sum_{i=1}^{N_A} \sum_{j>i}^{N_B} \ln(1 + \lambda f_{AB}(\mathbf{r}_i, \mathbf{r}_j)), \qquad \lambda \in [0, 1]. \tag{14}$$

where $f_{AB}(\mathbf{r}_i, \mathbf{r}_j) = e^{-\beta w_{AB}(\mathbf{r}_i, \mathbf{r}_j)} - 1$, it is easily verified that the first and second order corrections to the free energy are now

$$\beta F_1^{ex} = -4\pi N x_A x_B \rho \int_0^\infty g_{AB}^{(0)}(r) f_{AB}(r) r^2 dr \tag{15}$$

and

$$\beta F_2^{ex} = 2\pi N x_A x_B \rho \int_0^\infty g_{AB}^{(0)}(r) f_{AB}^2(r) r^2 dr - \frac{1}{2}\left\langle \left(\beta W'_{AB} - \langle \beta W'_{AB} \rangle\right)^2 \right\rangle_0, \tag{16}$$

where $g_{AB}^{(0)}(r)$ is the pair distribution function between A and B particles in the additive reference system (where $w_{AB}(r) \equiv 0$).

A special case of non-additive binary mixtures was considered by Pelissetto and Hansen in the context of colloid-polymer mixtures [6]. They used a reference mixture where particles of opposite species do not interact ("two fluid" system), i.e. $v_{AB}^{(0)}(r) \equiv 0$. In that case the perturbation $w_{AB}(r)$ includes the total coupling between A and B particles. Because of this, the expressions for F_1^{ex} and F_2^{ex} simplify considerably [6]; in particular F_2^{ex} only requires knowledge of the reference ("two fluid") pair distribution functions $g_{AA}^{(0)}(r)$ and $g_{BB}^{(0)}(r)$. In the Appendix we derive the formal expression for the third order term F_3^{ex}, which in this particular case only requires knowledge of the "two fluid" pair and triplet distribution functions $g_{\alpha\alpha}^{(0)}(\mathbf{r}_1, \mathbf{r}_2)$ and $g_{\alpha\alpha\alpha}^{(0)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$ ($\alpha = A$ or B). Although lengthy, a numerical evaluation of F_3^{ex} appears feasible in this case, if the triplet distribution functions are replaced by their Kirkwood superposition approximations [17] for hard sphere particles (e.g. colloids) or the convolution approximation [18, 17] for soft core particles (e.g. polymers). Work along these lines is planned for the future.

In the more general case where the two components of the mixture are already coupled in the reference system ($v_{AB}^{(0)}(r) \neq 0$), the explicit expression for the second order term (16) involves two, three, and four-body distribution functions and is intractable in practice. Moreover the "local compressibility" approximation [3] cannot easily be generalised to the multi-component case. For that reason we have restricted the free energy calculations for non-additive mixtures to first order in section 4

4 Applications

The application of the Mayer function perturbation theory will be restricted to the case where the reference potentials $v_{\alpha\beta}^{(0)}(r)$ are simply additive hard spheres interactions

$$v_{\alpha\beta}^{(0)}(r) = \begin{cases} \infty, & r < \sigma_{\alpha\beta} = (\sigma_A + \sigma_B)/2 \\ 0, & r > \sigma_{\alpha\beta} \end{cases} , \tag{17}$$

where σ_α is the diameter of particles of species α, while the perturbation will be a repulsive step function (or "shoulder")

$$w_{\alpha\beta}(r) = \begin{cases} \varepsilon_{\alpha\beta}, & \sigma_{\alpha\beta} < r < \sigma_{\alpha\beta}(1 + \Delta_{\alpha\beta}) \\ 0, & r > \sigma_{\alpha\beta}(1 + \Delta_{\alpha\beta}) \end{cases} , \tag{18}$$

where the $\varepsilon_{\alpha\beta}$ are positive energies. We will consider both finite steps and the limit of infinite steps, which amounts to an increase of the hard-core diameters from $\sigma_{\alpha\beta}$ to $\sigma_{\alpha\beta}(1 + \Delta_{\alpha\beta})$.

A severe test of the Mayer function perturbation theory is provided by the one-component hard sphere system characterised by the initial-core diameter σ

(reference system) and the final diameter $\sigma(1+\Delta)$ ($\varepsilon \to \infty$). The corresponding Mayer function is simply

$$f(r) = \begin{cases} -1, & \sigma < r < \sigma(1+\Delta) \\ 0, & r > \sigma(1+\Delta) \end{cases} . \tag{19}$$

This amounts to increasing the initial (reference) packing fraction from $\eta = \pi\rho\sigma^3/6$ to $\eta' = \eta(1+\Delta)^3$.

The properties of hard sphere systems are known to a high degree of accuracy for any packing fraction both in the fluid and in the solid phases. In the fluid the free energy is calculated from the Carnahan-Starling equation of state [19], while the pair distribution function is accurately represented by the Verlet-Weis semi-empirical modification of the analytic solution of the Percus-Yevick equation [20, 17]. The free energy of the FCC solid phase may be derived from Hall's equation of state up to close-packing [21, 22], while the pair distribution functions were taken from MC data and the fits in ref [23].

Figure 1 shows the excess free energy per particle as a function of packing fraction η', as calculated from second order perturbation theory for $\Delta = 0.05$ which correspond to a 16% increase in packing fraction relative to the reference fluid! The agreement between the perturbation theory predictions and the known "exact" results for the free energy is surprisingly good in the fluid phase, but deteriorates in the solid phase, so that the predicted freezing transition is shifted towards too large packing fractions. The second order correction is significantly smaller than the first order correction term. For the particular case where the Mayer function is given by eq. (19), the first (non-fluctuation) contribution to F_2^{ex} in eq. (10) is positive and exactly one half of the first order correction F_1^{ex}, while

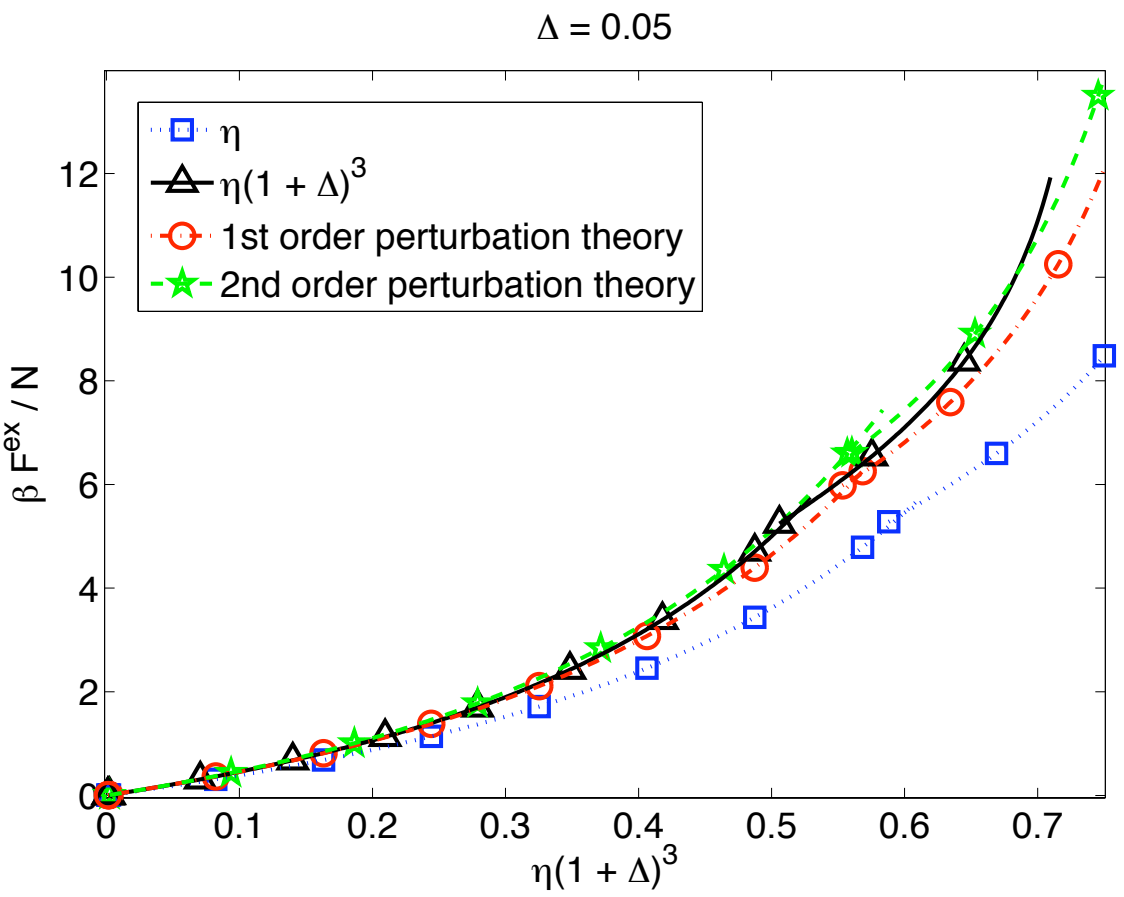


Figure 1: The excess free energy per particle vs. packing fraction $\eta' = \eta(1+\Delta)^3$ for $\Delta = 0.05$. Results are shown for the solid and fluid branches. The "exact" free energies are shown by the full line with triangles, the reference free energy by the dotted line with squares. The first and second order perturbation results are the dash dotted line with circles and the dashed line with stars

the fluctuation contribution is by definition negative. When evaluated within the "local compressibility" approximation it significantly reduces the total second order correction. At even larger values of Δ, the convergence is found to be slower, as expected. Nevertheless, even for $\Delta = 0.1$, second order perturbation theory yields good results for the free energy of the fluid (relative error less than 10% at $\eta' = 0.5$), but the results for the solid deteriorates rapidly as η' increases.

The conclusion to be drawn from this test-case is that the Mayer function per-

turbation theory truncated after second order yields reliable free energies even in the extreme case of a singular perturbation. For moderate values of the range Δ of the perturbation, satisfactory results are obtained when the expansion is truncated after first order; the corresponding free energy lies systematically slightly below the "exact" values. This is exactly the opposite of the Zwanzig perturbation theory where the free energy is bounded above by the first order series (Gibbs-Bogoliubov inequality). We have however no proof that the first order Mayer function expansion provides an exact lower bound.

The second system we have investigated is that of a binary mixture of spheres of diameters σ_A and σ_B (size ratio $\xi = \sigma_A/\sigma_B \leq 1$) with a repulsive step energy ε_{AB} and width Δ_{AB} between unlike particles (see eqs. (17) and (18)). We first consider the case of a symmetric non-additive mixture, with $\sigma_A = \sigma_B = \sigma$, $\Delta_{AB} = \Delta$ and $\varepsilon_{AB} = \varepsilon \to \infty$. This system has been examined earlier [15] using the semi-empirical equation of state of Barboy and Gelbart [24], and Monte Carlo data are available for the case $\Delta = 0.2$ [25]. As expected, non-additivity drives fluid-fluid phase separation above a critical packing fraction.

The phase diagram predicted by first order perturbation theory is compared in figure 2 to Amar's MC data. The agreement is seen to be excellent. As Δ is increased, the critical packing fraction is expected to drop [15].

The perturbation theory predictions for the critical reduced density as a function of Δ are compared in figure 3 to the earlier predictions based on the Barboy-Gelbart equation of state [15]. The two curves are seen to be close for $0 < \Delta < 1$. For the large non-additivity of $\Delta = 1$, the two curves are close to the scaled particle result of Mazo and Bearman [26], while for $\Delta = 0.2$, the prediction of the perturbation theory is in better agreement with the MC-results than the predic-

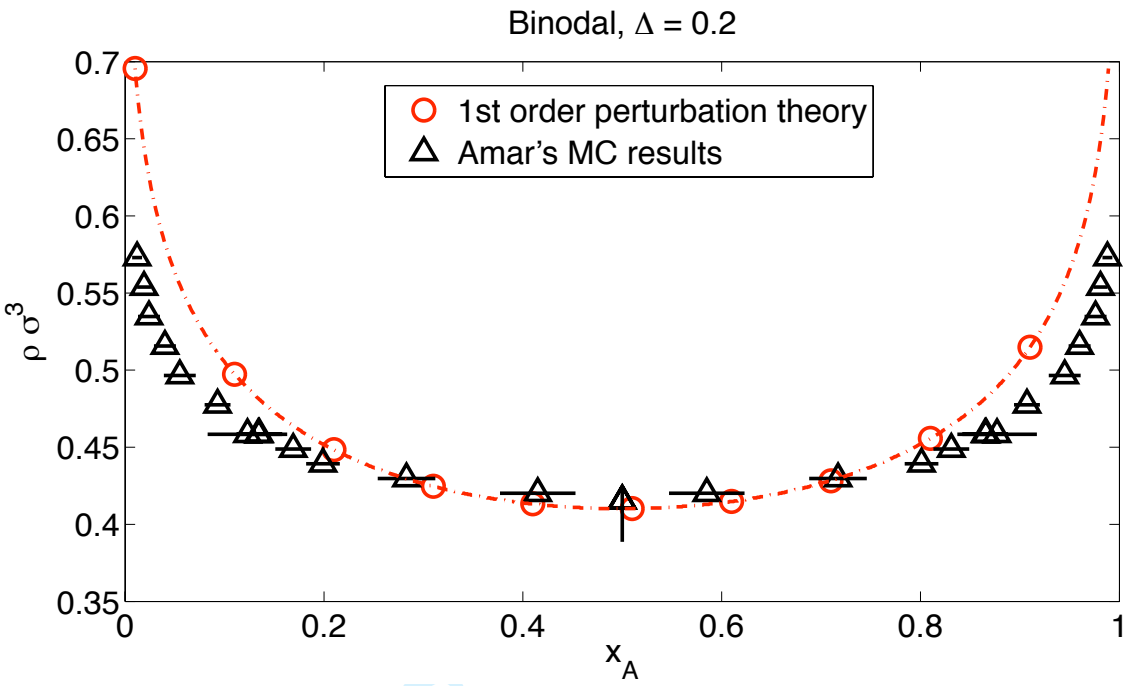


Figure 2: Binodal (density vs. concentration) as predicted from first order perturbation theory (circles and dashed curve) for $\xi = 1$ and $\Delta = 0.2$, compared to Amar's MC results (triangles with error bars)

tion from the Barboy-Gelbart equation.

We next turn our attention to the case of a symmetric binary mixture with a finite repulsive step (ε, Δ) between unlike particles. This system is no longer athermal, but the phase diagram now depends on reduced temperature $T^* = k_B T/\varepsilon$.

The results of first order perturbation theory for $\Delta = 0.2$ are summarised in the 3 frames of figure 4, which shows cuts (x_A, η), (η, T^*) and (x_A, T^*) of the coexistence surface. The trends are as expected; in particular the critical packing fraction increases as T^* increases. We are not aware of any previous study of the system for comparison.

We have also carried out first order perturbation calculations for non-additive

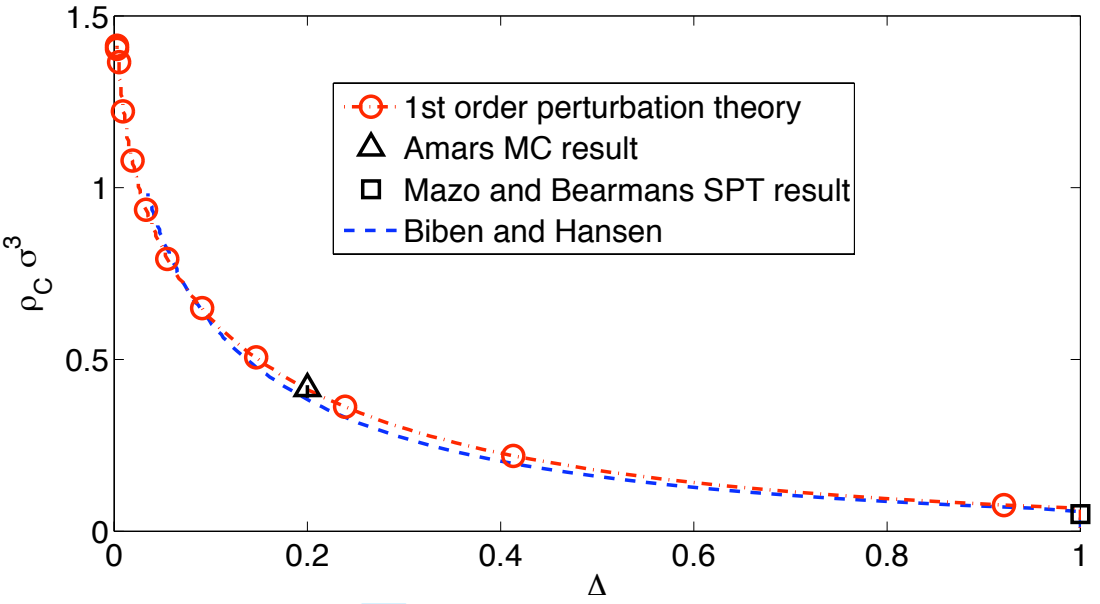


Figure 3: Critical reduced density $\rho_c\sigma^3$ vs. non-additivity parameter Δ for the symmetric non-additive hard sphere mixture. The dash-dotted curve with circles represents the results of first order perturbation theory. The dashed curve is based on the Barboy-Gelbart equation of state [15], the triangle is Amar's MC result [25], while the square is the scaled particle prediction of Mazo and Bearman [26]

asymmetric binary mixtures characterised by $\xi = \sigma_A/\sigma_B \ll 1$ and Δ ($\varepsilon = \infty$). The free energy of the additive reference system was derived from the binary hard sphere mixture equation of state of Mansoori et al. [27], while the required pair distribution function $g_{AB}(r)$ was taken from the solution of the PY equation [28]. Examples of the reduced excess free energies f vs. the concentration x_A of small spheres at fixed packing fraction η, and of f vs. η for fixed x_A are shown in figure 5, where they are compared to the predictions of a recent theory for non-additive hard spheres due to Santos et al. [29]. Agreement between the two very different theories is reasonable. Note that for the choosen parameters, $\xi = 0.2$ and $\Delta = 0.2$, the binary mixture is expected to phase separate into A-rich and A-poor mixtures

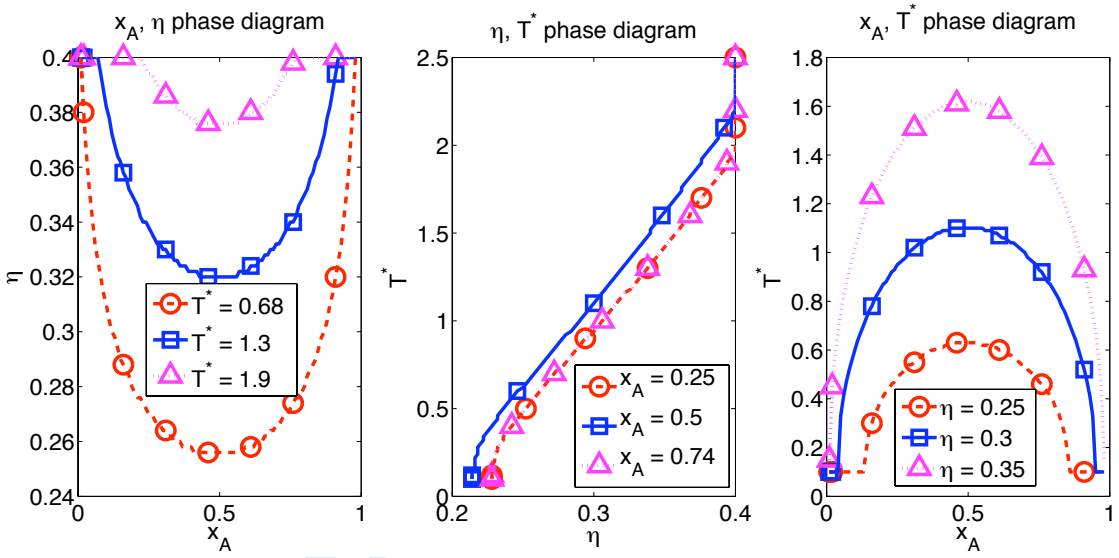


Figure 4: Three cuts through the phase diagram in temperature T - packing fraction η - composition $x_A = N_A/(N_A + N_B)$ space. The non-additivity parameter of the system is $\Delta = 0.2$.

[15, 30], as is easily checked from the stability limit (spinodal line):

$$\left(\frac{\partial \mu_A}{\partial \rho_A}\right)\left(\frac{\partial \mu_B}{\partial \rho_B}\right) - \left(\frac{\partial \mu_A}{\partial \rho_B}\right)^2 = 0. \tag{20}$$

In fact, for such an asymmetric mixture ($\xi = 0.2$), a much smaller value of Δ is sufficient to drive phase separation [15].

5 Conclusions

We have shown that a simple modification of standard thermodynamic perturbation theory, which focuses on the Mayer f-function, rather than the perturbation potential w itself, is successful in dealing with short-range, finite or infinite repulsive interactions. The convergence of the perturbation series for the free energy appears to be good, at least in the fluid phase and truncation after the first or-

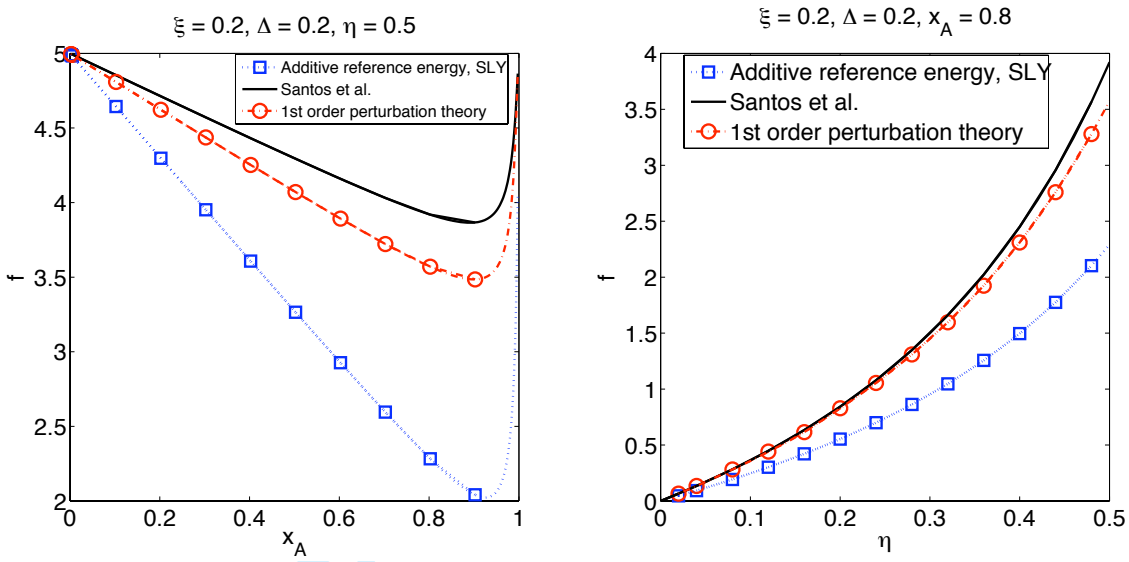


Figure 5: Reduced excess free energies per particle vs. concentration x_A at $\eta = 0.5$ (left) and vs. total packing fraction η at $x_A = 0.8$ (right), for the asymmetric binary mixture with $\xi = 0.2$ and $\Delta = 0.2$

der correction yields satisfactory results compared to known exact or simulation data.

The most interesting application is to highly asymmetric, non-additive binary mixtures (cf. eq. (18), with $\xi = \sigma_A/\sigma_B \ll 1$). A previous calculation [15], based on the semi-empirical Barboy-Gelbart equation-of-state [24], showed that the critical Δ required to drive phase separation decreases with ξ, and appears to go to zero (corresponding to additive hard spheres) around $\xi = 0.2$. This finding must be reconciled with the known behaviour of the Asakura-Oosawa model [16], which corresponds to the $\xi \to 0$ limit (ideal polymers being modelled as point particles), for a fixed, finite value of Δ. In fact, the free volume calculation of Lekkerkerker et al. [31] predicts a critical value $\Delta \sim 0.4$ to drive phase separation in that limit. This implies that somewhere in the interval $0 < \xi \lesssim 0.2$, the critical Δ must rise from zero towards its value for $\xi = 0$. We are planning to extend the present perturbation theory to support this conjecture of a non-monotonic variation of Δ

with size ratio ξ.

Appendix: Third Order Correction to the Free Energy of a Binary Mixture without A-B Interaction in the Reference System

In the case of a two-component system with no cross interaction in the reference system (i.e. $v_{AB}^{(0)}(r) \equiv 0$), the total perturbation potential is

$$\beta W(\lambda) = \sum_{i=1}^{N_A} \sum_{j=1}^{N_B} w_{AB,\lambda}(|\mathbf{r}_i - \mathbf{r}_j|) \tag{21}$$

The first and second order corrections were calculated by Pelissetto and Hansen in [6]. The third order term in the perturbation series (equation (3)) is

$$\frac{1}{3!}\Big(\langle \beta W''' \rangle + 3\big[\langle \beta W' \beta W'' \rangle - \langle \beta W' \rangle \langle \beta W'' \rangle\big] + \langle (\beta W' - \langle \beta W' \rangle)^3 \rangle\Big) \tag{22}$$

The first term $\langle \beta W''' \rangle$ is just

$$\langle \beta W''' \rangle = N_A N_B \langle w_2(|\mathbf{r}_1 - \mathbf{s}_1|) \rangle = 4\pi N x_A x_B \rho \int w_2(r) r^2 dr. \tag{23}$$

The first part of the second term, $\langle \beta W' \beta W'' \rangle$, can be worked out to be

$$\begin{aligned} \langle \beta W' \beta W'' \rangle \;=\; & 4\pi N x_A x_B \rho \int w_0(r) w_1(r) r^2 dr + \\ & + N_A \rho_B^2 \int d\mathbf{s_1} d\mathbf{s_2} w_0(s_1) w_1(s_2) g_{BB}^{(0)}(|\mathbf{s}_1 - \mathbf{s}_2|) + \\ & + N_B \rho_A^2 \int d\mathbf{r_1} d\mathbf{r_2} w_0(r_1) w_1(r_2) g_{AA}^{(0)}(|\mathbf{r}_1 - \mathbf{r}_2|) + \\ & + \rho_A^2 \rho_B^2 \int d\mathbf{r_1} d\mathbf{r_2} \int d\mathbf{s_1} d\mathbf{s_2} w_0(|\mathbf{r}_1 - \mathbf{s}_1|) w_1(|\mathbf{r}_2 - \mathbf{s}_2|) g_{AA}^{(0)}(|\mathbf{r}_1 - \mathbf{r}_2|) g_{BB}^{(0)}(|\mathbf{s}_1 - \mathbf{s}_2|) \end{aligned} \tag{24}$$

The second part of the second term, $\langle\beta W'\rangle\langle\beta W''\rangle$, is

$$\langle\beta W'\rangle\langle\beta W''\rangle = 16\pi^2 N^2 x_A x_B \rho^2 \int\int w_0(r_1) w_1(r_2) r_1^2 dr_1 r_2^2 dr_2 \tag{25}$$

What is left to calculate is

$$\begin{aligned}\left\langle \left(\beta W' - \langle\beta W'\rangle\right)^3 \right\rangle &= \left\langle (\beta W')^3 \right\rangle - 3\langle\beta W'\rangle\left\langle (\beta W')^2 \right\rangle + 2\langle\beta W'\rangle^3 = \\ &= \left\langle (\beta W')^3 \right\rangle - 3\langle\beta W'\rangle\left(\left\langle (\beta W')^2 \right\rangle - \left\langle \beta W' \right\rangle^2\right) - \langle\beta W'\rangle^3.\end{aligned} \tag{26}$$

The only term that hasn't been worked out yet is the first one,

$$\left\langle (\beta W')^3 \right\rangle = \sum_{i=1}^{N_A}\sum_{j=1}^{N_B}\sum_{k=1}^{N_A}\sum_{l=1}^{N_B}\sum_{m=1}^{N_A}\sum_{n=1}^{N_B}\left\langle w_{AB,0}(|\mathbf{r}_i - \mathbf{s}_j|) w_{AB,0}(|\mathbf{r}_k - \mathbf{s}_l|) w_{AB,0}(|\mathbf{r}_m - \mathbf{s}_n|)\right\rangle \tag{27}$$

This tedious sum will be worked out in 9 steps. The first step is to work out the term with $i = k = m$ and $j = l = n$. This term is simply

$$(i): \qquad N_A N_B \left\langle [w_{AB,0}(|\mathbf{r}_1 - \mathbf{s}_1|)]^3 \right\rangle = 4\pi N x_A x_B \rho \int [w_{AB,0}(r)]^3 r^2 dr \tag{28}$$

The second case is that with three equal indices for the A-particles and exactly one pair of equal indices for the B-particles. There are three such groups of terms, one with $j = l$, one with $j = n$ and one with $l = n$, hence the factor 3 below.

$$\begin{aligned}(ii): \qquad & 3N_A N_B (N_B - 1)\left\langle [w_{AB,0}(|\mathbf{r}_1 - \mathbf{s}_1|)]^2 w_{AB,0}(|\mathbf{r}_1 - \mathbf{s}_2|)\right\rangle = \\ = \qquad & 3N_A \rho_B^2 \int d\mathbf{s}_1 d\mathbf{s}_2 [w_{AB,0}(s_1)]^2 w_{AB,0}(s_2) g_{BB}^{(0)}(|\mathbf{s}_1 - \mathbf{s}_2|) \\ = \quad & 3N_A \rho_B^2 \left(\int d\mathbf{s}_1 [w_{AB,0}(s_1)]^2 \int d\mathbf{s}_2 w_{AB,0}(s_2) + \int \tfrac{d\mathbf{k}}{(2\pi)^3} [\hat{w}_{AB,0}(k)]^3 \hat{h}_{BB}^{(0)}(k) \right)\end{aligned} \tag{29}$$

The third case is the one with all A-particle indices equal, but no B-particle in-

dices equal: $i = k = m$, $j \neq l \neq n$, $j \neq n$.

$$(iii): \quad N_A N_B (N_B-1)(N_B-2)\big\langle w_{AB,0}(|\mathbf{r}_1-\mathbf{s}_1|)w_{AB,0}(|\mathbf{r}_1-\mathbf{s}_2|)w_{AB,0}(|\mathbf{r}_1-\mathbf{s}_3|)\big\rangle =$$
$$= \quad N_A\rho_B^3 \int d\mathbf{s}_1 d\mathbf{s}_2 d\mathbf{s}_3 w_{AB,0}(s_1)w_{AB,0}(s_2)w_{AB,0}(s_3)g^{(0)}_{BBB}(\mathbf{s}_1,\mathbf{s}_2,\mathbf{s}_3) \qquad (30)$$

Case (iv) is just case (ii) with A and B interchanged:

$$(iv): \quad 3N_A(N_A-1)N_B\big\langle [w_{AB,0}(|\mathbf{r}_1-\mathbf{s}_1|)]^2 w_{AB,0}(|\mathbf{r}_2-\mathbf{s}_1|)\big\rangle =$$
$$= \quad 3\rho_A^2 N_B \int d\mathbf{r}_1 d\mathbf{r}_2 [w_{AB,0}(r_1)]^2 w_{AB,0}(r_2) g^{(0)}_{AA}(|\mathbf{r}_1-\mathbf{r}_2|)$$
$$= \quad 3\rho_A^2 N_B \left(\int d\mathbf{r}_1 [w_{AB,0}(r_1)]^2 \int d\mathbf{r}_2 w_{AB,0}(r_2) + \int \tfrac{d\mathbf{k}}{(2\pi)^3} [\hat{w}_{AB,0}(k)]^3 \hat{h}^{(0)}_{AA}(k) \right) \qquad (31)$$

The fifth case has one pair of equal A-indices and one pair of equal B-indices. There are 3×3 such groups of terms, hence the factor 9 below:

$$(v): \quad 9N_A(N_A-1)N_B(N_B-1)\big\langle [w_{AB,0}(|\mathbf{r}_1-\mathbf{s}_1|)]^2 w_{AB,0}(|\mathbf{r}_2-\mathbf{s}_2|)\big\rangle = \qquad (32)$$
$$= \quad 9\rho_A^2\rho_B^2 \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{s}_1 d\mathbf{s}_2 [w_{AB,0}(|\mathbf{r}_1-\mathbf{s}_1|)]^2 w_{AB,0}(|\mathbf{r}_2-\mathbf{s}_2|) g^{(0)}_{AA}(|\mathbf{r}_1-\mathbf{r}_2|) g^{(0)}_{BB}(|\mathbf{s}_1-\mathbf{s}_2|)$$

Case (vi) has one equal pair of A-indices, but no equal B-indices and therefor needs to be multiplied by a factor 3.

$$(vi): \quad 3N_A(N_A-1)N_B(N_B-1)(N_B-2)\big\langle w_{AB,0}(|\mathbf{r}_1-\mathbf{s}_1|)w_{AB,0}(|\mathbf{r}_1-\mathbf{s}_2|)w_{AB,0}(|\mathbf{r}_2-\mathbf{s}_3|)\big\rangle =$$
$$= \quad 3\rho_A^2\rho_B^3 \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{s}_1 d\mathbf{s}_2 d\mathbf{s}_3 w_{AB,0}(|\mathbf{r}_1-\mathbf{s}_1|)w_{AB,0}(|\mathbf{r}_1-\mathbf{s}_2|)w_{AB,0}(|\mathbf{r}_2-\mathbf{s}_3|) \times$$
$$g^{(0)}_{AA}(|\mathbf{r}_1-\mathbf{r}_2|) g^{(0)}_{BBB}(\mathbf{s}_1,\mathbf{s}_2,\mathbf{s}_3) \qquad (33)$$

Appendix

Case (vii) is just case (iii) with A and B interchanged:

$$(vii): \quad N_A(N_A-1)(N_A-2)N_B\big\langle w_{AB,0}(|\mathbf{r}_1-\mathbf{s}_1|)w_{AB,0}(|\mathbf{r}_2-\mathbf{s}_1|)w_{AB,0}(|\mathbf{r}_3-\mathbf{s}_1|)\big\rangle =$$
$$= \quad \rho_A^3 N_B \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 w_{AB,0}(r_1)w_{AB,0}(r_2)w_{AB,0}(r_3)g^{(0)}_{AAA}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3) \qquad (34)$$

Case $(viii)$ is just case (vi) with A and B interchanged:

$$(viii): \quad 3N_A(N_A-1)(N_A-2)N_B(N_B-1)\big\langle w_{AB,0}(|\mathbf{r}_1-\mathbf{s}_1|)w_{AB,0}(|\mathbf{r}_2-\mathbf{s}_1|)w_{AB,0}(|\mathbf{r}_3-\mathbf{s}_2|)\big\rangle =$$
$$= \quad 3\rho_A^3\rho_B^2 \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{s}_1 d\mathbf{s}_2 w_{AB,0}(|\mathbf{r}_1-\mathbf{s}_1|)w_{AB,0}(|\mathbf{r}_2-\mathbf{s}_1|)w_{AB,0}(|\mathbf{r}_3-\mathbf{s}_2|)\times$$
$$g^{(0)}_{AAA}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)g^{(0)}_{BB}(|\mathbf{s}_1-\mathbf{s}_2|) \qquad (35)$$

And finally, case (ix) has no equal A-indices and no equal B-indices:

$$(ix): \quad N_A(N_A-1)(N_A-2)N_B(N_B-1)(N_B-2)\times$$
$$\big\langle w_{AB,0}(|\mathbf{r}_1-\mathbf{s}_1|)w_{AB,0}(|\mathbf{r}_2-\mathbf{s}_2|)w_{AB,0}(|\mathbf{r}_3-\mathbf{s}_3|)\big\rangle =$$
$$= \quad \rho_A^3\rho_B^3 \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{s}_1 d\mathbf{s}_2 d\mathbf{s}_3 w_{AB,0}(|\mathbf{r}_1-\mathbf{s}_1|)w_{AB,0}(|\mathbf{r}_2-\mathbf{s}_2|)w_{AB,0}(|\mathbf{r}_3-\mathbf{s}_3|)\times$$
$$\cdot g^{(0)}_{AAA}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)g^{(0)}_{BBB}(\mathbf{s}_1,\mathbf{s}_2,\mathbf{s}_3). \qquad (36)$$

References

[1] J.D. van der Waals, Thesis, Amsterdam (1873)

[2] R.W. Zwanzig, *J. Chem. Phys.*, **22**, 1420 (1954)

[3] J.A. Barker and D. Henderson, *J. Chem. Phys.*, **47**, 2856 (1967); J.A. Barker and D. Henderson, *Rev. Mod. Phys.*, **48**, 587 (1976)

[4] H.C. Andersen, J.D. Weeks, and D. Chandler *Phys. Rev. A*, **4**, 1597 (1971); J.D. Weeks, D. Chandler, and H.C. Andersen *J. Chem. Phys.*, **54**, 5237 (1971)

[5] J. M. Kincaid, G. Stell, and E. Goldmark, *J. Chem. Phys.*, **65**, 2172 (1976)

[6] A. Pelissetto and J.P. Hansen, *Macromolecules*, **39**, 9571 (2006)

[7] J.A. Barker, *Proc. Roy. Soc. A*, **241**, 547 (1957)

[8] D. Henderson and J.A. Barker, *J. Chem. Phys.*, **49**, 3377 (1968)

[9] D. Henderson and P.J. Leonard, *Proc. Nat. Acad. Sc. USA*, **68**, 2354 (1971); see also W. R. Smith, *Mol. Phys.* **22**, 1058 (1971)

[10] H.C. Longuet - Higgins, *Proc. Roy. Soc. A*, **205**, 247 (1951)

[11] D. Young, *J. Chem. Phys.*, **58**, 1647 (1973)

[12] B.J. Alder, *Ann. Rev. Phys. Chem.*, **24**, 325 (1973)

[13] P. Bolhuis and D. Frenkel, *J. Phys. Condens. Matter*, **9**, 381 (1997)

[14] E. Brindeau, R. Levant, and J.P. Hansen, *Phys. Lett.*, **60A**, 424 (1977)

[15] T. Biben and J. P. Hansen, *Physica A*, **235**, 142 (1997)

[16] S. Asakura and F. Oosawa, *J. Polymer. Sci.*, **33**, 183 (1958)

[17] J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids*, 3rd edition (Academic Press, Amsterdam, 2006)

[18] S. Ichimaru, *Phys. Rev. A*, **2**, 494 (1970)

[19] N. F. Carnahan and K.E. Starling, *Chem. Phys.*, **51**, 635 (1969)

[20] L. Verlet and J.J. Weis, *Phys. Rev. A*, **5**, 939 (1972)

[21] K. R. Hall, *J. Chem. Phys.*, **57**, 2252 (1971)

[22] J. J. Weis, *Mol. Phys.*, **28**, 187 (1974)

[23] Y. Choi, T. Ree and F.H. Ree, *J.Chem. Phys.*, **95**, 7548 (1991)

[24] B. Barboy and W.M. Gelbart, *J. Chem. Phys.*, **71**, 3053 (1979)

[25] J.G. Amar, *Mol. Phys.*, **67**, 739 (1989)

[26] R.M. Mazo and R.J. Bearman, *J. Chem. Phys.*, **93**, 6694 (1990)

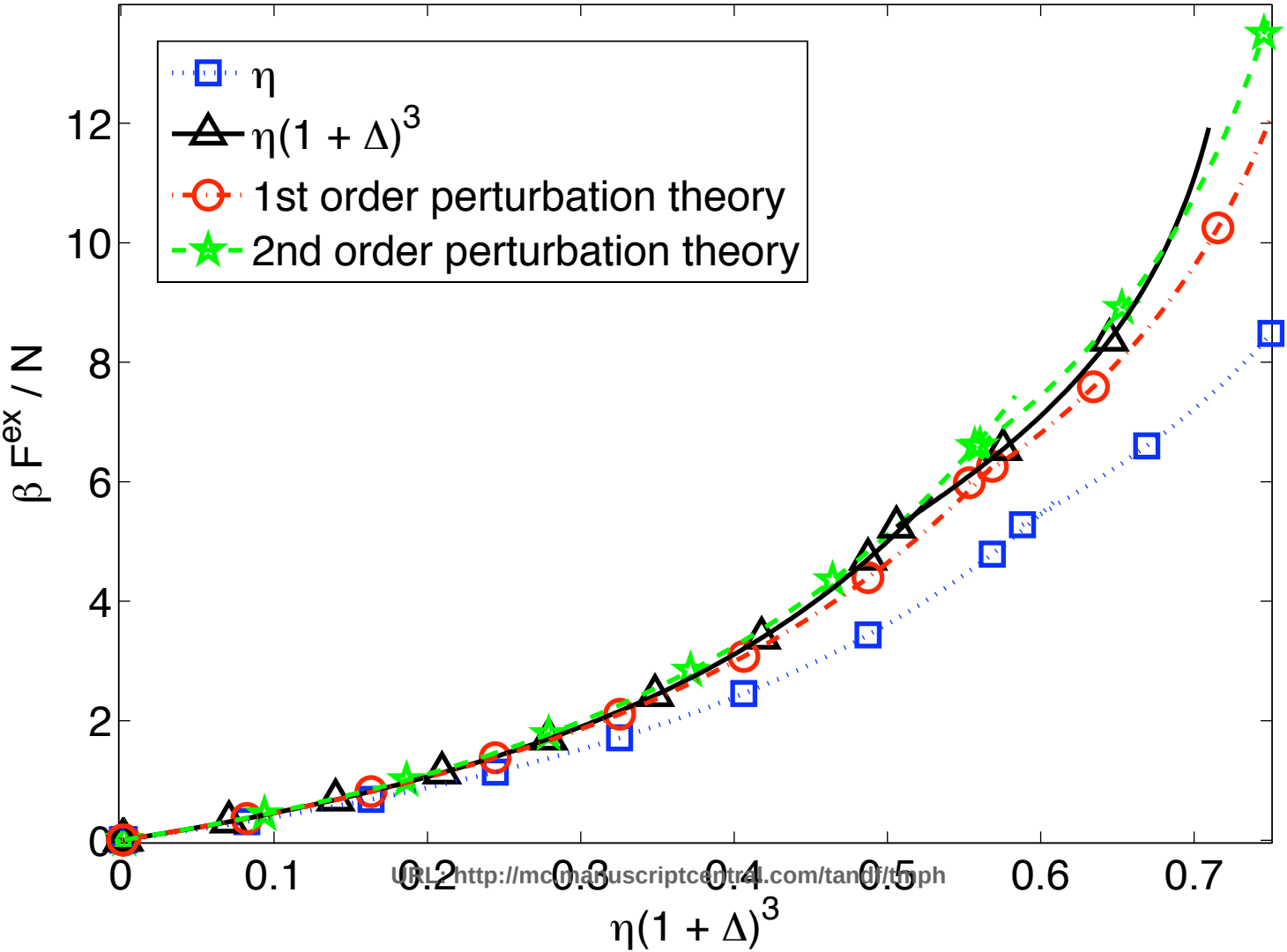
[27] G.A. Mansoori, N.F. Carnahan, K.F. Starling and T.W. Leland, *J. Chem. Phys.*, **54**, 1523 (1971)

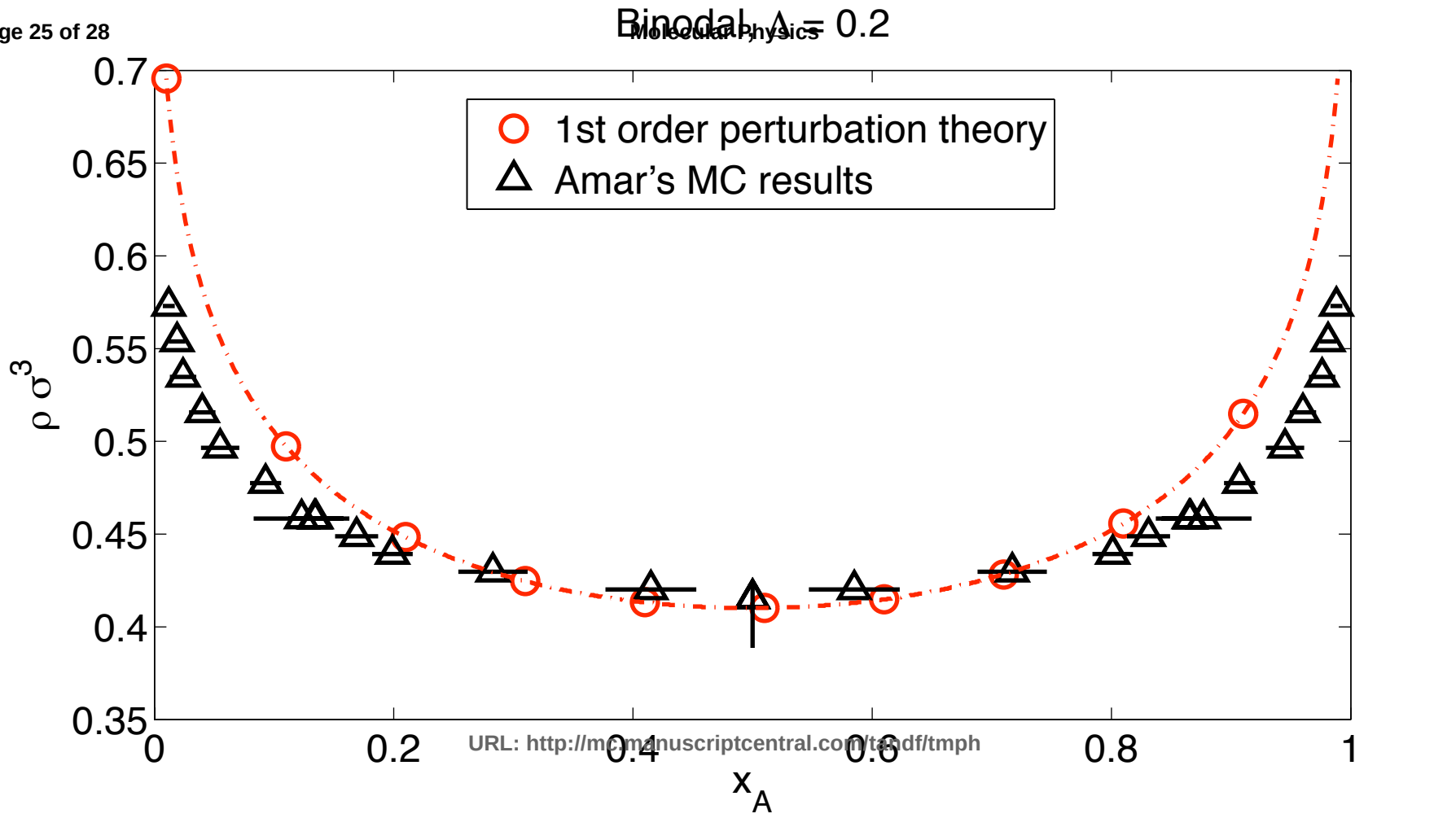
[28] G. Kahl and G. Pastore, *J. Phys. A Math. Gen.*, **24**, 299 (1991)

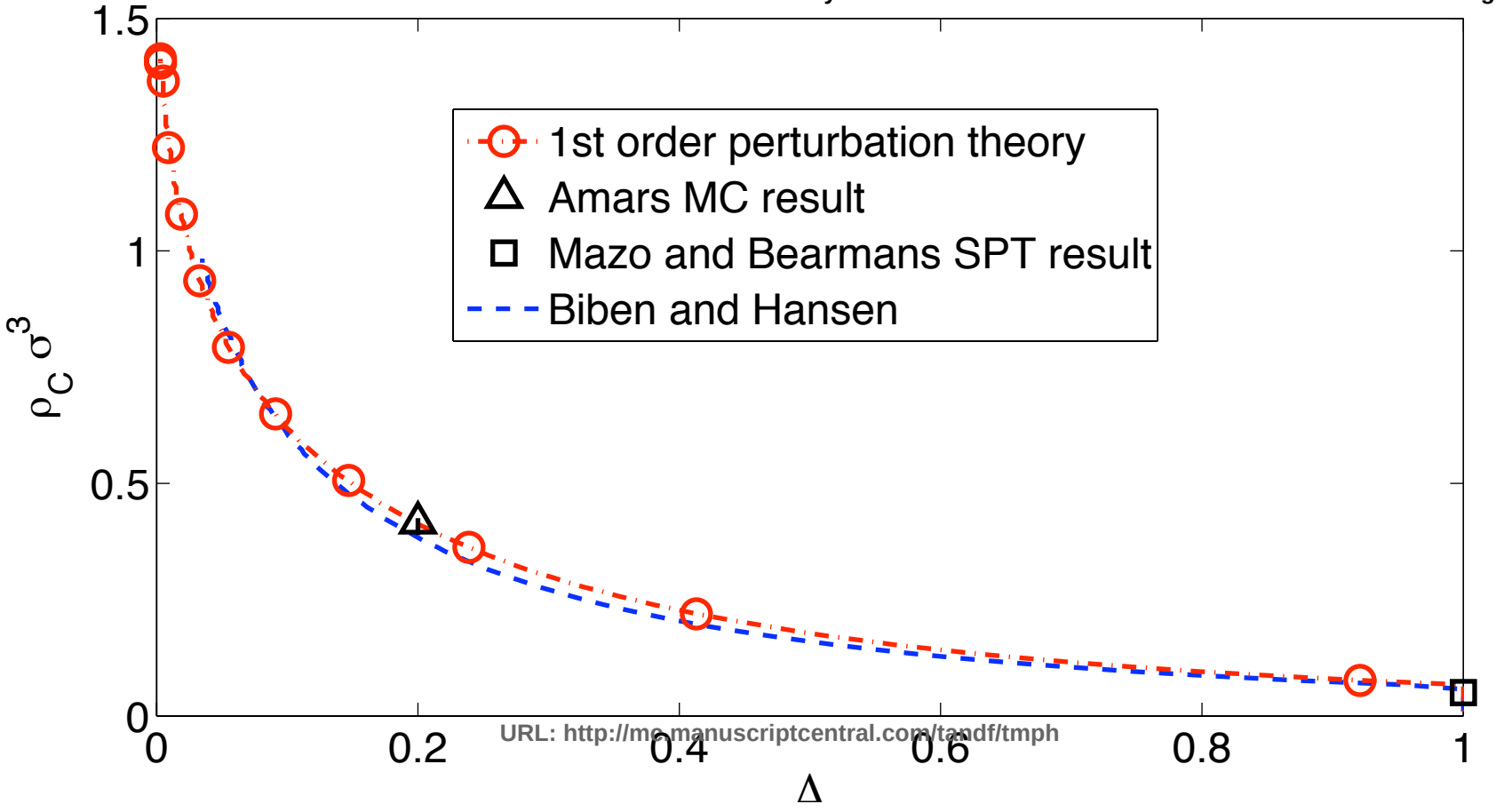
[29] A. Santos, M. López de Haro and S.B. Yuste, *J. Chem. Phys.*, **122**, 024514 (2005)

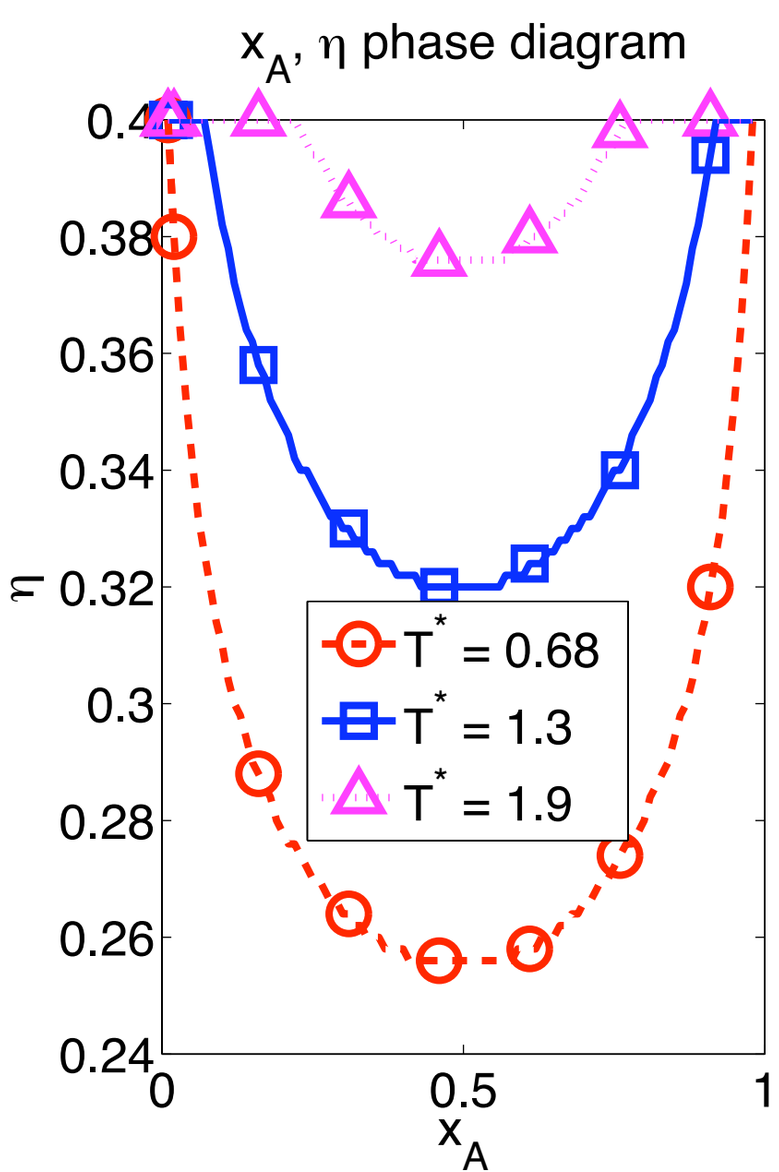
[30] M. Dijkstra, *Phys. Rev. E*, **58**, 7523 (1998)

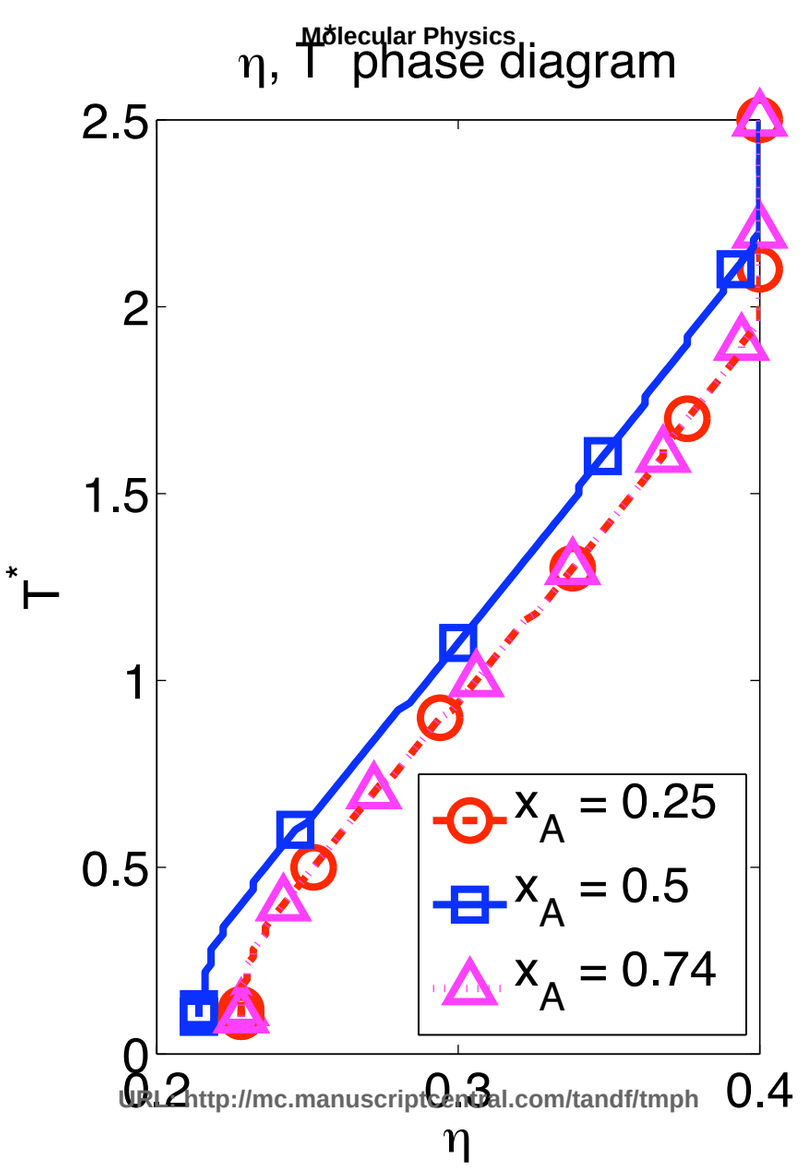
[31] H.N.W. Lekkerkerker, W.C.K. Poon, P.N. Pusey, A. Stroobants and P.B. Warren, *Europhys. Lett.*, **20**, 559 (1992)

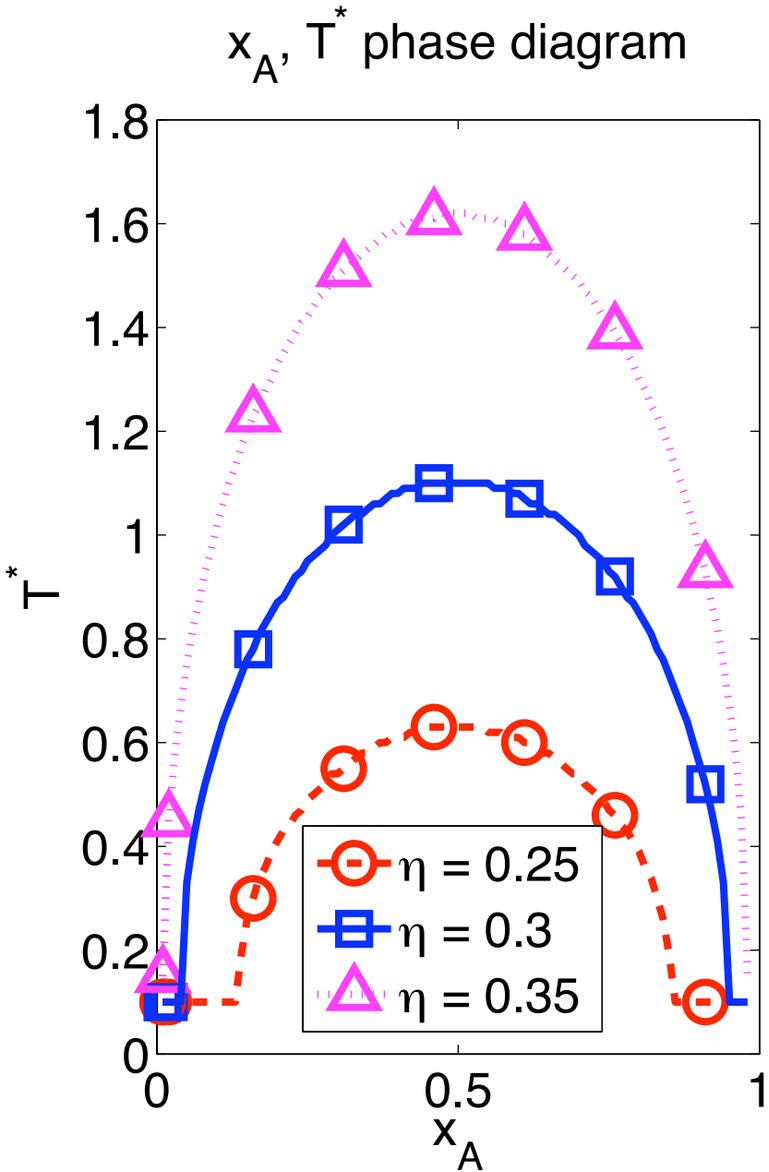


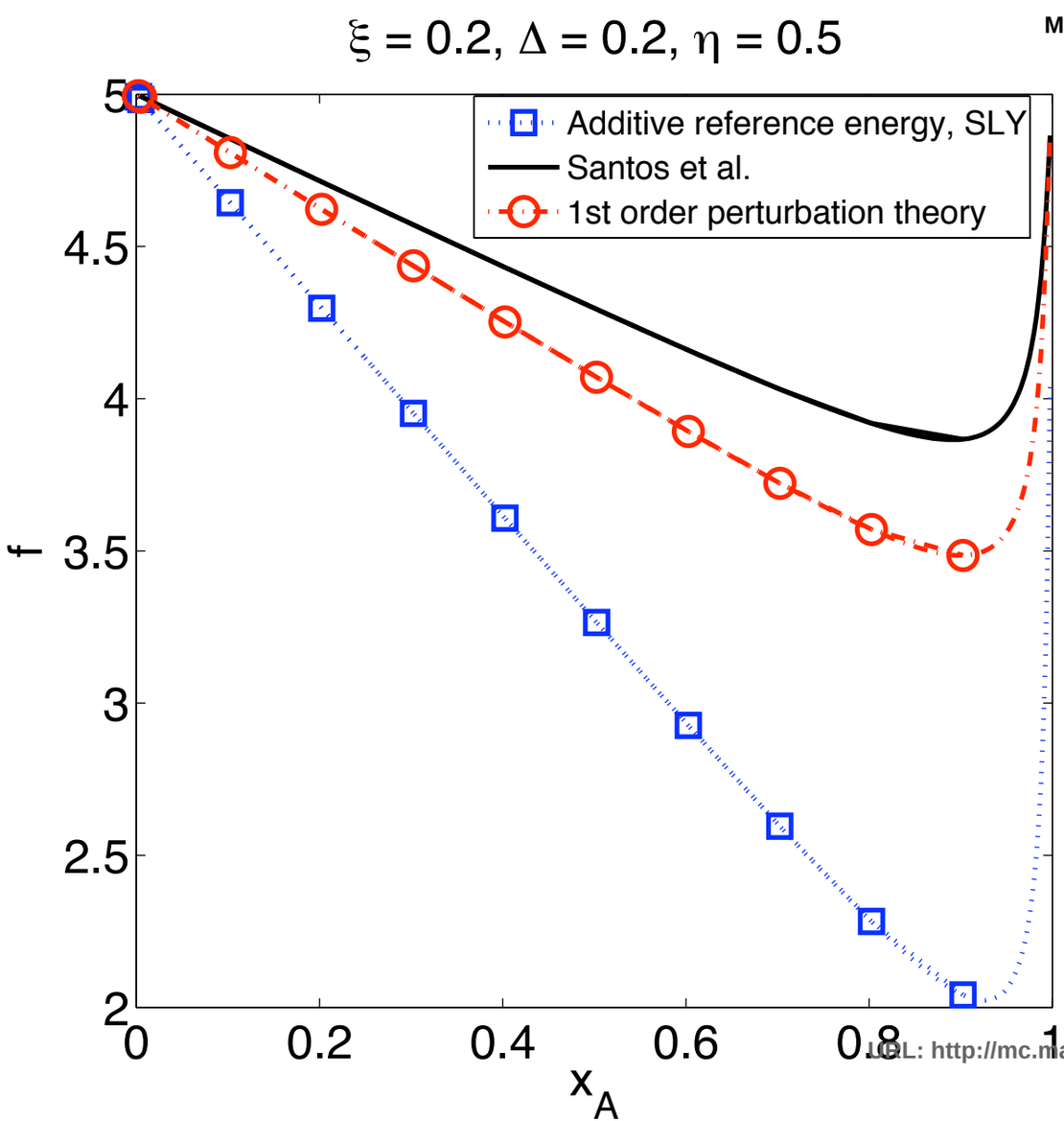


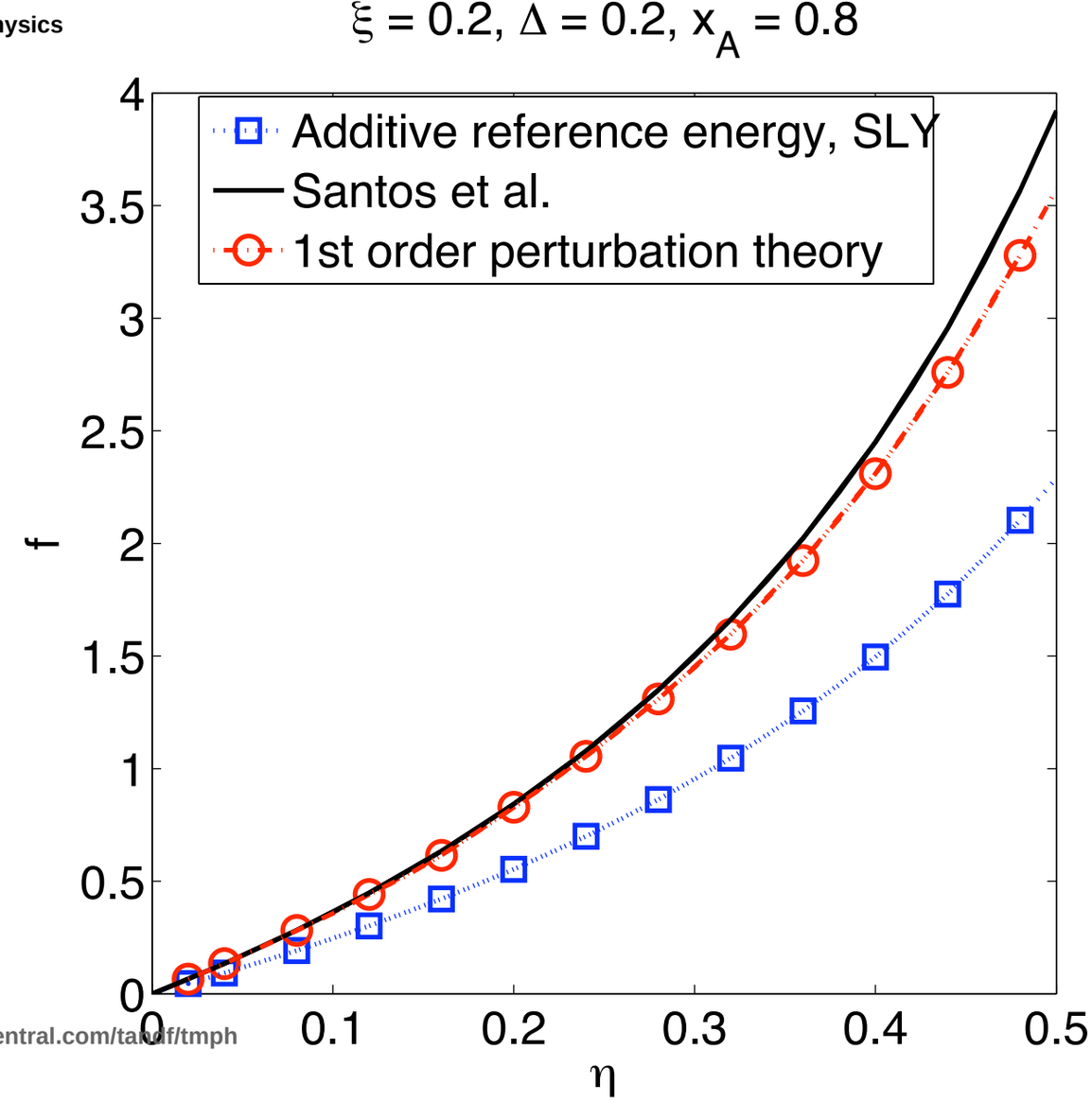



x_A, η phase diagram
η
x_A
$T^* = 0.68$
$T^* = 1.3$
$T^* = 1.9$


η, T^* phase diagram
T^*
η
$x_A = 0.25$
$x_A = 0.5$
$x_A = 0.74$


x_A, T^* phase diagram
T^*
x_A
η = 0.25
η = 0.3
η = 0.35


ξ = 0.2, Δ = 0.2, η = 0.5
Additive reference energy, SLY
Santos et al.
1st order perturbation theory
f
x_A
0
0.2
0.4
0.6
0.8
1
2
2.5
3
3.5
4
4.5
5


ξ = 0.2, Δ = 0.2, x_A = 0.8
Additive reference energy, SLY
Santos et al.
1st order perturbation theory
f
η
0
0.1
0.2
0.3
0.4
0.5
0
0.5
1
1.5
2
2.5
3
3.5
4