Stability of the iterative solutions of integral equations as one phase freezing criterion

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A recently proposed connection between the threshold for the stability of the iterative solution of integral equations for the pair correlation functions of a classical fluid and the structural instability of the corresponding real fluid is carefully analyzed. Direct calculation of the Lyapunov exponent of the standard iterative solution of hypernetted chain and Percus-Yevick integral equations for the one-dimensional (1D) hard rods fluid shows the same behavior observed in 3D systems. Since no phase transition is allowed in such 1D system, our analysis shows that the proposed one phase criterion, at least in this case, fails. We argue that the observed proximity between the numerical and the structural instability in 3D originates from the enhanced structure present in the fluid but, in view of the arbitrary dependence on the iteration scheme, it seems uneasy to relate the numerical stability analysis to a robust one-phase criterion for predicting a thermodynamic phase transition.

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I. INTRODUCTION

When studying the structure and thermodynamics of classical fluids, one is often faced with the task of solving the nonlinear integral equation which stems out of the combination of the Ornstein-Zernike equation and an approximate relation between pair potential and correlation functions (the closure) [1]. Integral equations can be generally written in the form

$$\gamma(r)=A\gamma(r), \tag{1}$$

where $\gamma(r)\in S$ may be the total correlation function $h(r)$, the direct correlation function $c(r)$, or a combination of the two, S is a set of a metric space of functions, and $A:S\to S$ is a nonlinear operator mapping S into itself.

Numerical analysis of integral equations suggests the use of the following combination

$$\gamma(r)=h(r)-c(r), \tag{2}$$

since γ is a much smoother function than h or c, especially in the core region.

It has been pointed out by Malescio and co-workers [2–4] that, amongst the different numerical schemes that one may choose to solve (1), the *simple iterative scheme of Picard* plays a special role. Picard's scheme consists in generating successive approximations to the solution through the relationship

$$\gamma_{n+1}=A\gamma_n, \tag{3}$$

starting from some initial value γ_0. If the sequence of successive approximations $\{\gamma_n\}$ converges toward a value $\gamma^\star$, then $\gamma^\star$ is a fixed point for the operator A, i.e., it is a solution of Eq. (1), $\gamma^\star=A\gamma^\star$. Banach' s fixed point theorem (see chapter 1 in Ref. [5] especially theorem 1.A) states that, given an operator $A:S\to S$, where S is a closed nonempty set in a complete metric space, the simple iteration (3) may converge towards the only fixed point in S (A is k contractive) or it may not converge (A is nonexpansive). So the simple iterative method can be used to signal a fundamental change in the properties of the underlying operator.

The operator A will, in general, depend on the thermodynamic state of the fluid. In order to determine the properties of the operator at a given state we can proceed as follows. First, we find the fixed point $\gamma^\star$ using a numerical scheme (more refined than the Picard's) capable of converging in the high density region. Next, we perturb the fixed point with an arbitrary initial perturbation $\delta_0(r)$ so that

$$A(\gamma^\star+\delta_0)\simeq A\gamma^\star+\left.\frac{\partial A}{\partial\gamma}\right|_{\gamma^\star}\delta_0=\gamma^\star+M\delta_0, \tag{4}$$

where we have introduced the Floquet matrix M. Now $\delta_1=M\delta_0$ may be considered as the new perturbation. We then generate the succession $\{\delta_n\}$ where

$$\delta_n=M\delta_{n-1}. \tag{5}$$

If the succession converges to zero then the operator A is k contractive, if it diverges the operator is nonexpansive. Malescio and co-workers call $\{\delta_n\}$ *fictitious dynamics* and associate it to the resulting fate of the initial perturbation the nature of the *structural equilibrium* of the fluid. If the succession converges to zero they say that the fluid is *structurally stable* and *structurally unstable* otherwise. We will call ρ_{inst} the density where the transition between a structurally stable and unstable fluid occurs.

Following Malescio and co-workers it is possible to define a *measure* for the structural stability of the system as follows. We define

$$S_i=\frac{||M\delta_i(r)||}{||\delta_i(r)||}, \tag{6}$$

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where $||f(r)||=\sqrt{\Sigma_{i=1}^{N} f^2(r_i)}$ is the norm of a function f defined over a mesh of N points. We assume that the norm of the perturbation depends exponentially on the number of iterations

$$||\delta_n||=||\delta_0||2^{\lambda n}, \tag{7}$$

where λ is the Lyapunov exponent related to the fictitious dynamics. Then one can write the average exponential stretching of initially nearby points as

$$\lambda=\lim_{n\to\infty}\frac{1}{n}\log_2\left(\prod_{i=0}^{n-1} S_i\right). \tag{8}$$

Malescio and co-workers have calculated the dependence of λ on the density for various simple three-dimensional liquids (and various closures): hard spheres [2], Yukawa, inverse power, and Lennard-Jones potentials [3]. For all these systems they found that λ increases with the density and the density at which λ becomes positive, ρ_{inst}, falls close to the freezing density ρ_f of the fluid system. This occurrence leads them to propose this kind of analysis as a one-phase criterion to predict the freezing transition of a dense fluid and to estimate ρ_f. However, we think that there are some practical and conceptual difficulties with such one-phase criterion.

First of all, it does not depend only on the closure adopted but also on the kind of algorithm used to solve the integral equation. Indeed, different algorithms give different ρ_{inst} and Malescio and co-workers choose to use as instability threshold for their criterion the one obtained using Picard algorithm, thus giving it a special status. However, it is hard to understand why the particular algorithm adopted in the solution of the integral equation should be directly related to a phase boundary.

Moreover, one would expect that the estimate of ρ_{inst} would improve in connection with improved closures. This is not the case, at least in the one-component hard-sphere fluid.

Even a more serious doubt about the validity of the proposed criterion comes from its behavior in one-dimensional systems. In this paper we present the same Lyapunov exponent analysis on a system of hard rods in one dimension treated using either the Percus-Yevick (PY) or the hypernetted chain (HNC) approximations. What we find is that the Lyapunov exponent as a function of density has the same behavior as that of the three-dimensional system (hard spheres): it becomes positive beyond a certain ρ_{inst}. Since it is known [6] that a one-dimensional fluid of hard rods does not have a phase transition, our result sheds some doubts on the validity of the proposed criterion.

II. TECHNICAL DETAILS

As numerical scheme to calculate the fixed point we used Zerah' s algorithm [7] for the three-dimensional systems and a modified iterative method for the hard rods in one dimension. In the modified iterative method input and output are mixed at each iteration

$$\gamma_{n+1}=A_{mix}\gamma_n=\alpha A\gamma_n+(1-\alpha)\gamma_n, \tag{9}$$

where α is a real parameter $0<\alpha<1$. Note that while for a nonexpansive operator A the Picard iterative method (3) needs not converge, one can prove convergence results on an Hilbert space for the modified iterative method with fixed α (see proposition 10.16 in Ref. [5]). In all the computations we used a uniform grid of $N=1024$ points with a spacing $\delta r=0.025$. Generally, we observed a marginal increase of ρ_{inst} by lowering N.

A method to find a Lyapunov exponent, equivalent but more accurate than the one of Malescio co-workers (8), goes through the diagonalization of the Floquet matrix. Note that in general this matrix is nonsymmetric, thus yielding complex eigenvalues. A Lyapunov exponent can then be defined as [8]

$$\lambda'=\log[\max_i(\sqrt{\mathrm{Re}(e_i)^2+\mathrm{Im}(e_i)^2})], \tag{10}$$

where e_i is the ith eigenvalue. In our numerical computations we always used Eq. (10) to calculate the Lyapunov exponents since it is explicitly independent from the choice of an initial perturbation.

We constructed the Floquet matrix in the following way [9]. In a Picard iteration we start from $\gamma(r)$, we calculate $c(r)$ from the closure approximation, we calculate its Fourier transform $\tilde{c}(k)$, we calculate $\tilde{\gamma}(k)$ from the OZ equation, and finally we antitransform $\tilde{\gamma}$ to get $\gamma'(r)$. For example for a three-dimensional system a PY iteration in discrete form can be written as follows:

$$c_i=(1+\gamma_i)(e^{-\beta\phi_i}-1), \tag{11}$$

$$\tilde{c}_j=\frac{4\pi\delta r}{k_j}\sum_{i=1}^{N-1} r_i\sin(k_j r_i)c_i, \tag{12}$$

$$\tilde{\gamma}_j=\rho\tilde{c}_j^2/(1-\rho\tilde{c}_j), \tag{13}$$

$$\gamma_i'=\frac{\delta k}{2\pi^2 r_i}\sum_{j=1}^{N-1} k_j\sin(k_j r_i)\tilde{\gamma}_j, \tag{14}$$

where $r_i=i\,\delta r$ are the N mesh points in r space, $k_j=j\,\delta k$ are the N mesh points in k space, with $\delta k=\pi/(N\delta r)$, $c_i=c(r_i)$, $\gamma_i=\gamma(r_i)$, $\tilde{c}_j=\tilde{c}(k_j)$, $\tilde{\gamma}_j=\tilde{\gamma}(k_j)$, and $\phi_i=\phi(r_i)$ is the interparticle potential calculated on the grid points. The Floquet matrix will then be

$$M_{ij}=\frac{\partial\gamma_i'}{\partial\gamma_j}=\sum_{m=1}^{N-1}\frac{\partial\gamma_i'}{\partial\tilde{\gamma}_m}\frac{\partial\tilde{\gamma}_m}{\partial\tilde{c}_m}\frac{\partial\tilde{c}_m}{\partial c_j}\frac{\partial c_j}{\partial\gamma_j}$$
$$=\frac{\delta r\,\delta k}{\pi}\left(\frac{r_j}{r_i}\right)(e^{-\beta\phi_j}-1)(D_{i-j}-D_{i+j}), \tag{15}$$

where

$$D_l=\sum_{m=1}^{N-1}\cos(k_m r_l)\left[\frac{2\rho\tilde{c}_m}{1-\rho\tilde{c}_m}+\left(\frac{\rho\tilde{c}_m}{1-\rho\tilde{c}_m}\right)^2\right]. \tag{16}$$

The HNC case can be obtained replacing in Eq. (15) $[\exp(-\beta\phi_j)-1]$ with $[\exp(-\beta\phi_j+\gamma_j)-1]$.

To derive the expression for the Floquet matrix valid for the one-dimensional system and consistent with a trapezoidal discretization of the integrals, we need to replace Eqs. (11) and (13) with

$$\tilde{c}_j = 2\,\delta r\left(\sum_{i=1}^{N-1}\cos(k_j r_i)c_i + \frac{1}{2}c_0\right), \tag{17}$$

$$\gamma_i' = \frac{\delta k}{\pi}\left(\sum_{i=1}^{N-1}\cos(k_j r_i)\tilde{\gamma}_j + \frac{1}{2}\tilde{\gamma}_0\right). \tag{18}$$

III. NUMERICAL RESULTS

We checked our procedure for a three-dimensional hard-spheres fluid and a Lennard-Jones fluid at a reduced temperature $T^*=2.74$. Our results, obtained using Eq. (10), were in good agreement with those of Malescio *et al.* [2,3] which used recipe (8) instead (another difference between our analysis and theirs is that we used for γ the indirect correlation function (2) while they were using the total correlation function h). For the Lennard-Jones fluid our results were indistinguishable from those of Malescio *et al.* [3]. We found a reduced instability density ρ^*_{inst} around 1.09 in the PY approximation and around 1.06 in the HNC approximation. For the three-dimensional hard-sphere fluid we found slightly larger (4%) values for ρ_{inst}. We found a $\eta_{inst}=\rho_{inst}\pi d^3/6$ of about 0.445 in the PY approximation and around 0.461 in the HNC approximation. We also checked the value corresponding to the Martynov-Sarkisov [10] closure and we found $\eta_{inst}=0.543$.

We feel that the differences are within what we can expect on the basis of small numerical differences in different implementations. We think that it is more worthy of notice that closures providing better structural and thermodynamic properties, like PY or MS do not provide a better value of η_{inst}.

We looked at the structure of the Floquet matrix too but from direct inspection we can conclude that it is not diagonally dominated.

Then, we have calculated the Lyapunov exponent (10) as a function of the density for a fluid of hard rods in one dimension using both PY and HNC closures. The results of the calculation are shown in Fig. 1 and Fig. 2. The curves show the same qualitative behavior as the ones for the three-dimensional fluid. From Fig. 1 we can see how the slope of the curves starts high at low densities and decreases rapidly with ρ. At high densities the Lyapunov exponent becomes zero at ρ_{inst}. As expected, to find the fixed point for $\rho \gtrsim \rho_{inst}$ it is necessary to choose $\alpha<1$ in the modified iterative scheme (9). Before reaching the instability threshold the curves show a rapid change in their slope at $\rho_c<\rho_{inst}$. Figure 2 shows a magnification of the region around ρ_c from which we are led to conclude that, within the numerical accuracy of the calculations, the slope of the curves $d\lambda'/d\rho$ undergoes a jump at ρ_c.

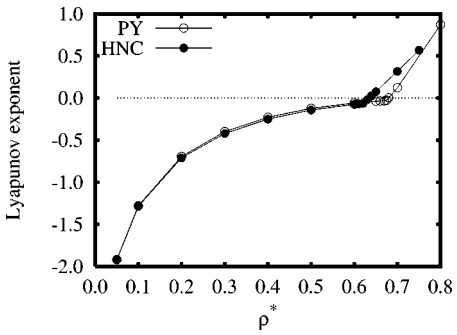

FIG. 1. For a fluid of hard rods in one dimension, we show the Lyapunov exponent as a function of the reduced density ($\rho^*=\rho\sigma$ where σ is the rods width) as calculated using the PY and the HNC closures.

IV. CONCLUSIONS

The fictitious dynamics associated to the iterative solution of an integral equation can signal the transition of the map of the integral equation from k contractive to nonexpansive. If the Lyapunov exponent is negative the map is k contractive, if it is positive the map is nonexpansive.

Since it is possible to modify, in an arbitrary way, the fictitious dynamics keeping the same fixed point, it is difficult to understand a deep direct connection between the stability properties of the map and a one-phase criterion for a thermodynamic transition.

Admittedly, the correlations shown by Malescio *et al.* are striking. We calculated the Lyapunov exponent as a function of the density for various fluids (hard spheres in one and three-dimensions and three-dimensional Lennard-Jones fluid) both in the HNC and PY approximations. For the three-dimensional fluids the instability density falls close to the freezing density ρ_f. For example, the Lennard-Jones fluid studied with HNC should undergo a freezing transition at $\rho^*\simeq 1.06$ or at $\rho^*\simeq 1.09$, if studied with PY , rather close to the freezing density $\rho_f^*\simeq 1.113$. For hard spheres ρ^*_{inst} is about 10% smaller than $\rho_f^*\sim 0.948$. The Hansen-Verlet ''rule'' states that a simple fluid freezes when the maximum of the structure factor is about 2.85 [11]. According to this rule the three-dimensional hard-spheres fluid studied with HNC should undergo a freezing transition at $\rho\simeq 1.01$ while when studied with PY the transition should be at $\rho\simeq 0.936$.

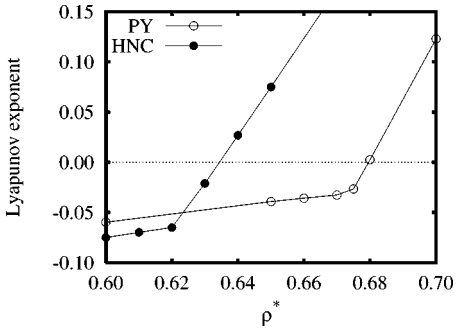

FIG. 2. We show a magnification of Fig. 1 in a neighborhood of the instability threshold.

The corresponding estimates obtained through ρ^*_{inst}, 0.879 (HNC) and 0.850 (PY) are poorer and, more importantly, are not consistent with the well known better performance of PY in the case of hard spheres.

In one dimension, a fluid of hard spheres (hard rods), cannot undergo a phase transition [6]. From Fig. 1 we see that the system still becomes structurally unstable. This can be explained by observing that the structural stability as defined by Malescio *et al.* is a property of the map A and in particular of the algorithm used to get the solution of the integral equation under study. As such, it is not directly related to the thermodynamic properties even at the approximate level of the theory (there is no direct relation between the contractiveness properties of A and the thermodynamics). It looks more reasonable that the increase of the correlations would be the common origin of the numerical instability of the Picard iteration and, whenever it is possible, of thermodynamic phase transitions.

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