Iterative solutions of integral equations and structural stability of fluids

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We argue that the threshold density of structural stability, ρ_{inst}, of a classical fluid can be determined from the Floquet matrix for the iterative form of the integral equation for the pair structure. A measure of the structural stability of the fluid is provided by the Lyapunov exponent related to the perturbed dynamics. The hypernetted-chain and Percus-Yevick equations yield, for hard spheres, a value of ρ_{inst} that is about 10% smaller than the freezing density. [S1063-651X(98)51104-X]

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A still open problem in equilibrium statistical mechanics is whether an intrinsic stability threshold of the dense fluid phase, which is expected to be close to the freezing density, can be deduced on the basis of one-phase criteria, i.e., without considering also the free energy of the solid. A well known such criterion is the Hansen-Verlet ''rule'' stating that a simple fluid freezes when the maximum of the structure factor is about 2.85 [1]. The configurational entropy also provides a measure of the structure which correlates well with freezing [2]. Other ''freezing criteria'' arise quite naturally from the properties of solutions of integral equations for the pair distribution function of the fluid [3], or from the instability of the iterative solutions for such equations [4]. In particular, Rosenfeld [4] showed that the stability limit of the hypernetted-chain (HNC) equation, with respect to its defining diagrammatic iteration loop, falls close to the freezing density for a large variety of interaction pair potentials. However, this semiempirical result did not allow one to define some functional of the given pair correlation function which identifies the stability property of the fluid structure *per se*. In this Rapid Communication we study the relation between the physical stability of a statistical system and the stability of the solution of the integral equations used to describe its equilibrium properties. We present a stability analysis that is based on the application of the Floquet matrix [5] (for the iterative form of the integral equation for the pair structure) on arbitrary perturbations and show that the Lyapunov exponent related to the corresponding dynamics provides a *measure* of the structural stability of the fluid. We focus on distribution-function theories [6,7] as those represented by the Percus-Yevick (PY) and HNC equations, but our analysis can be easily extended to other theoretical methods, such as the density functional theory (DFT). As a demonstration, we calculate the structural stability boundary of the hard-sphere fluid through the PY, HNC, and modified HNC (MHNC) equations.

Quite generally, integral equations can be written in the form:

$$f(r)=Af(r), \tag{1}$$

where $f(r)\in S$ describes the particle distribution of the system investigated, S is a set of a metric space, and $A:S\rightarrow S$ is an operator mapping S onto itself. Usually these equations cannot be solved analytically and thus one resorts to *iterative methods* which, in turn, occupy an important niche in modern mathematical physics. When applying the simple iterative method to Eq. 1, one generates, starting from some initial value f_0, successive approximations to the solution through the mapping

$$f_{n+1}=Af_n. \tag{2}$$

If the sequence of successive approximations $\{f_n\}$ converges towards a value f^*, then f^* is a fixed point for operator A, i.e., it is a solution of Eq. (1): $f^*=Af^*$. This procedure is the starting point of other more refined iterative methods. For example, a simple but effective technique to improve convergence is provided by linear relaxation which gives origin to the modified iterative method in which input and output are *mixed* at each iteration:

$$f_{n+1}=A_{mix}f_n=\alpha Af_n+(1-\alpha)f_n, \tag{3}$$

where α is a real parameter $0<\alpha<1$, which is kept constant or can be altered in some suitable way at each iteration.

Generally, the operator A of Eq. (1) describes how the values assumed by f over the whole system should be ''processed'' in order to determine f at the point considered. In particular, the nonlinear integral equations for fluids, which are obtained by supplementing the Ornstein-Zernike relation with some appropriate closure, i.e., an independent relation between the total $[h(r)]$ and the direct $[c(r)]$ correlation functions [6], have the form

$$f(r)=K[r,f(r)]+\int K[|\mathbf{r}-\mathbf{s}|,f(|\mathbf{r}-\mathbf{s}|)]f(s)d\mathbf{s}, \tag{4}$$

where $f(r)$ denotes one of the above mentioned correlation functions, typically $h(r)$, and K is a kernel that depends on the closure adopted. Equation (4) defines $f(r)$, i.e., the value of the function f at an arbitrary point of the system with spatial coordinate r, in terms of the values of f at *all* of the points of the system. Within the approximation inherent to the closure, this mathematical procedure appears as the counterpart of a physical process since every point of the system contributes, via mutual interactions, to determine the value

of f at a given point. As suggested by the fixed-point form of Eq. (1), at equilibrium there is a ''detailed balance'' between the local value of f and that resulting from the ''processing,'' represented mathematically by operator A, of the values that f assumes over the entire system. We assert that this condition is tantamount to a definition of *structural equilibrium* for the system investigated. In order to ascertain the nature of this equilibrium state let us suppose to perturb the equilibrium correlation function $f^*(r)$ by an arbitrary perturbation $\delta(r)$. The nonequilibrium distribution $f(r)=f^*(r)+\delta(r)$, is then ''processed'' by the operator A, and to first order in the perturbation it yields $M\delta(r)$, where the matrix $M=(\partial A/\partial f)|_{f^*}$ is the Floquet matrix acting on the perturbation vector (in numerical applications r is represented by a grid of N points, the function f is an N vector and A is an f-dependent $N\times N$ matrix). $M\delta$ may be considered, in turn, as a perturbation which, when processed by the system, gives origin to a new perturbation $MM\delta$, and so on. The successive processings thus generate a *fictitious dynamics* consisting of repeated applications of the Floquet matrix to the initial perturbation. The nature of the *structural equilibrium* of the system can be associated with this dynamics and with the resulting fate of the perturbation. It follows that the properties of operator A, on which the fictitious dynamics depends, are crucial as far as the structural stability of the fluid is concerned.

Generally, the operator A depends on one or more parameters, and when these parameters are changed, one can pass from regions in which the numerical procedure adopted to solve Eq. (1) does converge and the method is *stable*, to regions where the procedure does not converge and the method becomes *unstable*. The stability threshold may depend on the particular iterative method employed, a feature which surely contributed to cast heavy shadows on the physical meaning of the numerical instability. In order to clarify the relationship between structural and numerical stability, we resort to a mathematical result which is fundamental for our purposes. Banach's fixed-point theorem [8] states that, given an operator $A:S\rightarrow S$, where S is a closed nonempty set in a complete metric space with distance d, if A is k contractive [i.e., if $d(Ax,Ay)\leqslant kd(x,y)$ for all $x,y\in S$ and for a fixed k with $0\leqslant k<1$], then A has exactly one fixed point in S, i.e., Eq. (1) has one single solution, and the sequence of successive approximations defined through Eq. (2), which amounts to the simple iterative method, converges to the solution f^* for an arbitrary choice of the initial point f_0 in S. Under these conditions the above defined fictitious dynamics, and thus the structural equilibrium of the fluid, is stable. On the other hand, if A is nonexpansive (i.e., the above defined condition holds for $k=1$) the simple iterative method needs not converge while, according to a suitable generalization of Banach theorem (see [8]), the sequence of modified successive approximations constructed through Eq. (3) does converge to the fixed point of A.

Let us now interpret, in the light of the preceding considerations, the behavior of the numerical solution of the integral equations for the fluid structure in the high-density region. For simplicity, we suppose that A depends on some parameter ρ (e.g., the particle number density). It is a well-known feature that successive approximations, i.e., the simple iterative method, converge to the fixed point f^* (which in principle depends on ρ) only up to a value ρ_{inst}. As follows from the Banach fixed-point theorem this implies that for $\rho>\rho_{inst}$ operator A is no longer k contractive. Usually, one is interested in the solution of the integral equation rather than in the stability of the simple iterative method. Indeed, when this becomes unstable, the current attitude is to reduce, as far as possible, the region where the numerical solution is unstable through the adoption of other numerical techniques. For example, if at ρ_{inst} operator A changes from k contractive to nonexpansive the adoption of the modified iterative method Eq. (3) suffices to find the solution f^* of Eq. (1) beyond ρ_{inst} (though more refined methods may achieve convergence more rapidly). The importance of the stability threshold of the simple iterative method resides then in that it signals a fundamental change in the properties of operator A which is related, as specified before, to the structural stability of the fluid. This indication is lost when more refined methods are adopted.

It may be useful to observe that, though the mappings defined in Eqs. (2) and (3) have the same fixed point equation and thus the same fixed point f^*, the range of stability of f^* is different for the two operators. From the functional analysis results recalled above it follows that if A is nonexpansive then A_{mix} is k contractive (while, if A is k contractive, A_{mix} is *a fortiori* k contractive). Thus, if f^* is a stable fixed point for A, then it is also a stable fixed point for A_{mix}, but the opposite does not hold, namely, f^* may be a stable fixed point for A_{mix} though being an unstable fixed point for A. In the last case f^* satisfies the equilibrium condition, but the equilibrium state described is *structurally unstable* in the sense previously specified. Though we have considered in detail only the modified iterative method, a similar effect can be expected when ''forcing'' convergence through more refined techniques. The preceding point may be efficaciously illustrated with a simple example. Let us consider the well known one-dimensional logistic map [9], $x_{n+1}=F(x_n)=\mu x_n(1-x_n)$, and the following ''modified'' logistic map, $x_{n+1}=\alpha F(x_n)+(1-\alpha)x_n$, where $0<\alpha<1$. The logistic map follows a period-doubling route to chaos. Its attracting set evolves with μ as follows: for $0<\mu<1$ the map has a point attractor, $x_1=0$, which becomes unstable for $\mu=1$; here the fixed point $x_2=\mu-1/\mu$ becomes stable and remains so until $\mu=3$ where a bifurcation gives origin to a periodic attractor with period two. Through a series of successive pitchforklike bifurcations a chaotic attractor eventually appears. The ''modified'' logistic map shows a similar behavior but bifurcations are shifted towards higher values of μ. Upon focusing our attention on the point attractors, we note that the two maps have the same fixed-point equation, and, consequently, the same fixed points x_1 and x_2. However, the mixing procedure alters their range of stability: in particular, the stability of x_2 is extended beyond $\mu=3$ up to $\mu=\mu_1=(2+\alpha)/\alpha$, where the first bifurcation takes place.

A particularly well known application of integral equation theories in the statistical mechanics of fluids is the *analytic* solution of the PY equation for the hard-sphere fluid [6]. It is a well-established result [6] that the three-dimensional hard-sphere fluid undergoes a freezing transition for $\eta_f\simeq 0.49$, where $\eta=(\pi/6)\rho\sigma^3$ is the packing fraction in terms of the hard-sphere diameter σ. On the other hand, the analytical solution of the PY equation is well-behaved up to $\eta=1$,

where the pressure as calculated via both the virial and compressibility expressions diverges, and apparently shows no trace of the crystallization of the fluid. On this basis it might have been stated that the PY equation is unable to furnish any hint on the phase behavior of the hard-sphere fluid. However, one should consider that the analytical approach gives no information on the dynamical properties of the operator A relative to the PY equation, unless these are explicitly studied, e.g., through a linear stability analysis. For involved integral equations this may be hardly feasible by analytical means. On the other hand, the numerical iterative approach furnishes not only the solution of the equation (obviously within numerical accuracy) but, *when implemented through the simple iterative method*, reveals itself as an indicator of the structural stability of the system (within the accuracy of the closure adopted). In the case considered here, the simple iterative method has an upper stability threshold at $\eta_{inst} \simeq 0.43$. Calculations were performed using a grid of $N=1024$ points with spacing of 0.02σ; however, η_{inst} is rather insensitive to the mesh used and remains essentially the same even for much less accurate calculations with coarser grids. In analogy with the logistic map case considered above, when solving the PY equation through the modified iterative method, the stability threshold is shifted towards higher values of η, the smaller the parameter α the larger the shift observed. We note that the stability threshold of the simple iterative method is an indicator of the transition of the system investigated from a regime where it is structurally stable to a regime where it is *structurally unstable*, while at the freezing point the fluid becomes *thermodynamically unstable* (or *metastable*) with respect to the solid. Hence, η_{inst} and η_f are expected to be close but need not be identical.

It is interesting to compare the PY estimate of η_{inst} with that provided, for the hard-sphere fluid, by other closures (for which, however, only the numerical solution exists). We considered the HNC equation and two MHNC approaches that employ approximate functional expressions for the ''bridge function'' [10] [representing the sum of all elementary diagrams, $E(r)$], specifically those proposed by Verlet (V) [11] and by Martynov and Sarkisov (MS) [12]. We obtained $\eta_{inst}=0.43$, 0.44, 0.39, 0.52 for the PY, HNC, V, and MS approximations, respectively. The HNC estimate of η_{inst} is close to that provided by the PY equation, while the two MHNC schemes give quite different results. Since, as far as thermodynamical and structural quantities are concerned, the PY equation is, for hard spheres, more accurate than the HNC equation, while both MHNC approaches lead to improvements with respect to PY (and HNC) results, the above values of η_{inst} do not reflect in general the relative accuracy of the different closures for what concerns thermodynamical and structural quantities. In fact, these properties are related to $E(r)$, whereas the stability properties of the numerical solution depend on $\partial A/\partial f|_{f*}$ and, consequently, on the functional derivative $\partial E(r)/\partial f(r)$. In approximate theories, an expression for $E(r)$ may lead to accurate structural and thermodynamical quantities while not improving, or even worsening, the accuracy of $\partial E(r)/\partial f(r)$. It might be expected that the structural stability threshold ρ_{inst} (as defined above) for the MHNC integral equation, with the exact (but unknown) $E(r)$, is close to the freezing point ρ_f for the fluid. This can provide a constraint for approximations on $E(r)$.

Having substantiated the equivalence between the structural stability of the fluid and the numerical stability of Eq. (2), one might study how the last evolves with the density (and eventually is lost) through the standard method based on the analysis of the eigenvalues of the Floquet matrix. We applied this procedure for different closures (HNC, PY) and potentials (inverse-power potentials, Yukawa potential, etc.) and found, in agreement with [4], that even for densities much smaller than the stability threshold ρ_{inst} some eigenvalues of the Floquet matrix can assume values greater than 1 [13]. This can be explained by observing that when the matrix is not normal then in general one cannot find a orthonormal set of vectors, or even a pair of orthogonal eigenvectors. In fact, the N nonorthonormal eigenvectors do not always span the N-dimensional vector space and, consequently, the eigenvectors do not always form a complete set. As a result, the existence of eigenvalues greater than 1 does not necessarily imply a divergence of the perturbation upon repeated application of the matrix. Since the analysis of the eigenvalues of the Floquet matrix is not useful to predict the result of a repeated application of the matrix, this deserves a direct investigation. Thus, starting from an *arbitrary* (we tried a wide variety of functional forms) initial perturbation $\delta_0(r)$ of the fixed point $f^*(r)$, repeated applications of M generate the succession $\{\delta_n\}$, where $\delta_n = M\delta_{n-1}$. This succession either converges to zero or diverges, depending on whether the structural equilibrium of the fluid is stable (i.e., for $\rho<\rho_{inst}$) or unstable (i.e., for $\rho>\rho_{inst}$), respectively. We note that the Floquet matrix M is a functional of the solution of Eq. (1), f^*, and thus can be calculated also for $\rho>\rho_{inst}$ by employing numerical methods converging beyond ρ_{inst}. In particular, within the PY approximation for hard spheres M can be obtained from the corresponding analytic solution for any $\eta<1$. As expected, the stability boundary thus identified agrees very well (to within numerical uncertainty) with the stability limit obtained from the dynamic behavior of the simple iterative method. The procedure based on the Floquet matrix has, however, the obvious advantage that Eq. (1) can be solved using a numerical method that is both faster and less sensitive to the initial input as compared to the simple iterative method. Moreover, it makes possible to define, as shown below, a *measure* of the structural stability of the system.

The effect of repeated applications of the Floquet matrix on the initial perturbation δ_0 can be represented as follows:

$$\frac{\|\delta_n\|}{\|\delta_0\|}=\prod_{i=0}^{n-1} S_i, \tag{5}$$

where

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

and $\|f(r)\|=\sqrt{[\Sigma_{i=1}^{N} f^2(r_i)]}$ is the norm of a function f defined over a mesh of N points. Assuming that the norm of the perturbation depends exponentially (as long as it remains infinitesimal) on the number of iterations, i.e., $\|\delta_n(r)\| = \|\delta_0(r)\|2^{\lambda n}$, where λ is the Lyapunov exponent related to the perturbation dynamics, one can write the average exponential stretching of initially nearby points as

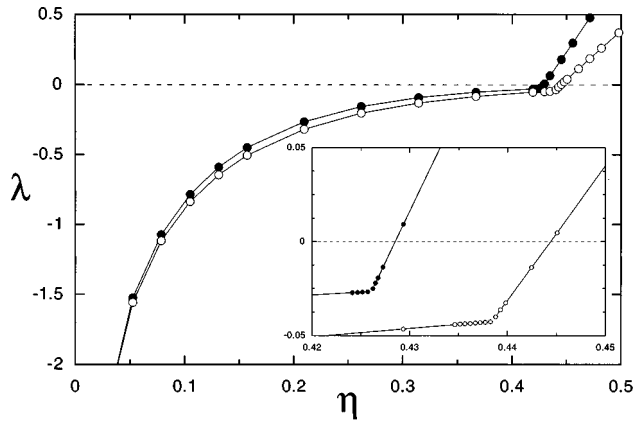

FIG. 1. The Lyapunov exponent λ plotted as a function of the packing fraction for the hard-sphere fluid, as estimated through the PY (solid circles) and HNC (open circles) equations. The inset shows a magnification of the sharp change of behavior in the region around η_c.

$$\lambda = \lim_{n\to\infty} \frac{1}{n} \log_2 \left(\prod_{i=0}^{n-1} S_i \right). \tag{7}$$

The actual number of iterations after which λ reaches its saturation value depends on the density, ranging from few tens at low density to few hundreds near the instability point. Though in principle the Lyapunov exponent depends on the initial perturbation $\delta_0(r)$, we found that wildly different forms of the initial perturbation lead to essentially identical values of λ. Consequently this quantity can provide a measure of the stability of the solution, and thus of the structural stability of the fluid.

We calculated λ for the hard-sphere fluid within the PY and HNC approximations. As shown in Fig. 1, as the density increases λ becomes less and less negative, thus signaling a less efficacious damping of the perturbation, i.e., a decrease of the stability of the fluid. The slope of the curve, initially quite steep, decreases rapidly with η so that the value $\lambda = 0$, corresponding to the loss of stability of the solution, might appear attainable only for very large values of η. However, at a density η_c, slightly smaller than η_{inst}, the curve exhibits a sudden increase of its steepness and, correspondingly, λ goes rapidly to zero on approaching η_{inst}. Note, on the qualitative side, that this behavior does not depend on the closure adopted. It thus appears evident that the fluid undergoes, *before* the loss of structural stability, a rather well-defined ''transition'' to a regime of rapidly deteriorating stability. The phenomenon is not a gradual one: in fact, as can be better appreciated from the inset in Fig. 1, two distinct branches, both linear but with different slope, meet at η_c. This feature is independent of the density of points, which suggests that the derivative $d\lambda/d\eta$ is discontinuous at η_c, at least within the limits of numerical accuracy of the calculation. From a dynamical point of view this behavior reflects the approaching to the incipient instability and the growing influence of a new attracting set (no longer a point attractor). In principle this phenomenon may be reflected in physical properties other than those concerning the structural stability of the fluid. While equilibrium properties do not exhibit any anomalous behavior in correspondence with this region, it is well known that simulation results show a sensible variation of dynamical properties at high densities: crystallization is preceded by a rapid, though gradual, fall of the diffusion coefficient and by a much sharper rise of the shear viscosity. The nature of the structural stability limit and its relation to freezing deserves further study which may lead to a physical definition of a stable fluid structure. Details of the present analysis, and applications to various potentials and integral equations, as well as an extension to the intermediate density region in the presence of an attractive component in the potential, will be presented elsewhere [13].

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