Structural stability of simple fluids and accuracy of integral-equation theories

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The ability to describe the structural stability of a fluid may represent a stringent test for the overall physical soundness of an integral-equation theory. The accuracy of some approximate closures of the Ornstein-Zernike equation is discussed in relation to the estimates of the density threshold of structural stability of the fluid that are obtained through an analysis of the iterative form of the integral equation. The connection with the random-close-packing threshold of hard spheres is also investigated.

Recently, the numerical instability at high densities of the iterative solution of integral equations for the fluid structure has been related to an intrinsic, structural stability threshold of the dense fluid phase [1]. In this paper, we surmise that the accuracy with which an integral equation is able to describe such a feature may actually represent an alternative ''benchmark''—with respect to other, more standard thermodynamical and structural quantities—for testing the reliability of the corresponding approximate closure. We explore this issue also in relation to the possibility of estimating, within an integral-equation theory, the density of random close packing (RCP) of a fluid of hard spheres.

The concept of structural stability emerges from an analysis of the form of integral equations used to describe local density correlations in a fluid. Typically, these equations are obtained by supplementing the Ornstein-Zernike (OZ) relation with an appropriate closure, i.e., an approximate, independent relation between the total correlation function $h(r)$ and the direct correlation function $c(r)$. In general, these equations can be synthetically written in the form

$$f(r) = Af(r), \qquad (1)$$

where $f(r) \in S$ describes the particle distribution function, S is a set of a metric space, and $A: S \rightarrow S$ is an operator mapping S onto itself. The fixed-point form of Eq. (1) suggests that the equilibrium state of the fluid is characterized by a ''detailed balance'' condition between the value of f at a given point r and that resulting from a nonlocal processing—that is mathematically represented by the nonlinear integral operator A—of the values of f over the entire system. In [1], the authors suggested that, within the approximation inherent to the closure, this condition is tantamount to a definition of *structural equilibrium*. The nature of this equilibrium condition can be associated with the fictitious dynamics that is generated through repeated applications of the Floquet matrix for the operator A to an arbitrary initial perturbation of the fluid structure [1]. From this analysis, it follows that the stability threshold of the simple iterative method, based on successive approximations to the solution of Eq. (1) that are obtained through the mapping

$$f_{n+1} = Af_n, \qquad (2)$$

is an indicator, within the accuracy of the chosen closure, of a structural transition of the system from a stable to an unstable regime. The resulting stability threshold ρ_{inst} is expected to be close to the freezing density ρ_f. However, the two densities do not need to coincide since, at the freezing point, the fluid becomes *thermodynamically* unstable with respect to the solid.

In [1], the stability threshold ρ_{inst} was calculated for a fluid of hard spheres within the hypernetted-chain (HNC) and Percus-Yevick (PY) approximations. The results were then compared with the freezing-point density. Somewhat surprisingly, the authors found that the estimates obtained for ρ_{inst} do not reflect the relative accuracy shown by the two closures in the prediction of other thermodynamical and structural quantities. In particular, the HNC estimate of ρ_{inst} turns out to be slightly closer to ρ_f than the PY one. Recently, this point was analyzed in more detail by investigating the stability of fluids interacting through inverse-power potentials of the form $\phi(r) \sim 1/r^n$ [2]. The HNC estimate of ρ_{inst} was found to be close to ρ_f for $n > 4$, while remaining reasonably accurate also for smaller values of n. On the contrary, as the steepness of the potential decreases, the PY result rapidly loses any correspondence with the (increasing) freezing density. Such a failure is more dramatic than the well-known lack of accuracy shown by the PY equation in the prediction of the structural properties of model systems with long-ranged potentials. One of the goals of this paper is to understand which feature may be responsible for this behavior.

As discussed in [1], the structural stability of the fluid is related to the Floquet matrix $M = (\partial A / \partial f)|_{f*}$, where $f*$ is the equilibrium distribution function. In order to compare the relative accuracy of integral equations, a considerable simplification can be achieved by considering the iterative procedure used to solve Eq. (1). One single iteration of the cycle is defined by the following operations: starting from some initial guess for $c(r)$, one calculates the Fourier transform $c(k)$ and then, through the OZ relation, $h(k)$. This quantity is Fourier inverted to obtain $h(r)$ and, finally, using an approximate closure $c(r) = c[h(r)]$, a new estimate for $c(r)$. Hence, a perturbation $\Delta c_n(r)$ of the nth estimate of the direct correlation function is tantamount to a perturbation $\Delta h_n(r)$ of the corresponding total correlation function, which, in turn, gives rise to a perturbation $\Delta c_{n+1}(r)$ of the

new estimate of $c(r)$. It is rather clear that the relevant quantity, as far as the stability of the solution is concerned, is the functional derivative $\partial c(r)/\partial h(r)$. In order to illustrate this point, let us consider the HNC and PY equations. The corresponding closures are $c(r)_{\text{HNC}} = -\beta u(r) + h(r) - \ln[1 + h(r)]$, and $c(r)_{\text{PY}} = [1 + h(r)][1 - e^{\beta u(r)}]$, where $\beta = 1/(k_B T)$ is the inverse temperature in units of the Boltzmann constant k_B, and $u(r)$ is the interparticle potential [3]. As is well known, both closures correctly yield the first-order term in the density expansion of the pair correlation function $g(r)$. Moreover, the PY equation, while neglecting a larger number of diagrams than the HNC approximation, yields more accurate results for the thermodynamical and structural properties of systems with short-ranged potentials. *A posteriori*, this result is explained by hypothesizing a mutual and fortuitous partial cancellation of the diagrams that are neglected in the PY approximation [3]. However, the importance of the additional diagrams included in the HNC equation becomes evident when one analyzes the expressions for the functional derivative $\partial c(r)/\partial h(r)$ which follow from the HNC and PY approximations, respectively:

$$\left(\frac{\partial c(r)}{\partial h(r)}\right)_{\text{HNC}} = \frac{h(r)}{1+h(r)}, \quad \left(\frac{\partial c(r)}{\partial h(r)}\right)_{\text{PY}} = 1 - e^{\beta u(r)}. \quad (3)$$

While the HNC derivative shows an explicit dependence on the density via the total correlation function, the PY expression does not. It thus follows that the PY ''response'' of the system to a weak perturbation of the structure is the same whatever the density. This is, of course, an unrealistic feature. We also note that, by letting $\rho \to 0$ in $[\partial c(r)/\partial h(r)]_{\text{HNC}}$, one recovers the PY result. Hence, we argue that the lower accuracy of the PY equation in estimating the structural stability threshold of the fluid is to be ascribed to the less flexible form of the corresponding expression for the functional derivative $\partial c(r)/\partial h(r)$ as far as the density dependence is concerned.

The analysis presented above offers a perspective for evaluating the overall reliability of an approximate integral closure. In fact, one is prompted to consider not only the accuracy with which the standard thermodynamical and structural quantities are estimated, but also the ability of the theory to describe the structural stability of the fluid. An approximate closure may actually yield a poor expression for the functional derivative $\partial c(r)/\partial h(r)$, while producing reasonably accurate estimates of the thermodynamics and pair structure.

As already remarked, although the stability threshold ρ_{inst} may be expected to be close to the freezing density ρ_f, the two quantities refer to distinct aspects, viz., the conditions of structural and thermodynamical stability, respectively. For a hard-core fluid, a quantity that is directly related to the intrinsic stability of the fluid structure is the maximum density achievable through a dense random-close-packed arrangement of the particles. This threshold coincides with the terminus of the thermodynamically metastable, overcompressed fluid branch. In the past, there have been efforts, based on the solution of a nonlinear integral equation for the singlet distribution function of an inhomogeneous fluid [4], to predict both the freezing and RCP densities within the same theoretical approach [5]. We show in the following that, within the
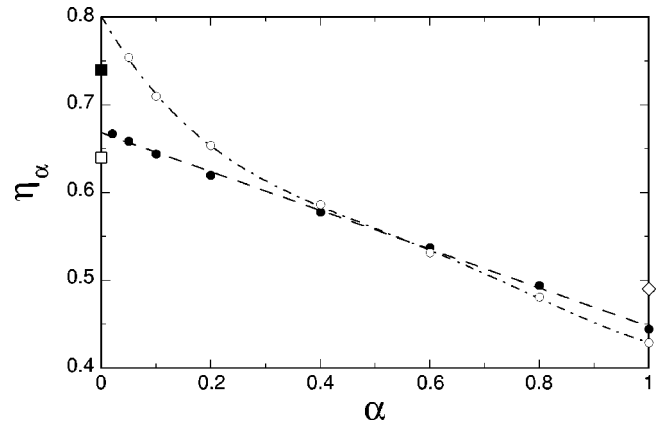

FIG. 1. Stability threshold η_α of the operator A_{mix} plotted as a function of α for hard spheres within the HNC (filled dots) and PY (open circles) approximations. The solid and open squares mark the close-packing and random-close-packing fraction, respectively. The open diamond identifies the freezing-point packing fraction.

present scheme, the RCP density can be related to the stability threshold of the *modified* iterative method:

$$f_{n+1} = A_{mix} f_n = \alpha A f_n + (1-\alpha) f_n, \quad (4)$$

where $0 < \alpha < 1$ is a real parameter. In this method, at each iteration the output $A f_n$ that would be obtained through the simple iterative method is mixed with the input function f_n. The smaller α, the smaller the fraction of the updated function $A f_n$ and the larger that of the previous estimate f_n. It is common experience that this method often converges even when the simple one does not. Indeed, although the mappings defined in Eqs. (2) and (4) 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 [1]. In fact, if f^* is a stable fixed point for A, then it is also a stable fixed point for $A_{mix} = \alpha A + (1-\alpha)I$, where I is the identity operator. The opposite does not hold, namely, f^* may be a stable fixed point for A_{mix} while being an unstable fixed point for A. In the latter case, f^* satisfies the equilibrium condition but the equilibrium state described is structurally unstable, since an arbitrary initial perturbation grows under repeated applications of the Floquet matrix for the operator A.

Figure 1 shows the stability threshold η_α of the operator A_{mix}, plotted as a function of α, for hard spheres within the HNC and PY approximations. The stability threshold is expressed in terms of the packing fraction $\eta = (\pi/6)\rho\sigma^3$, where σ is the hard-sphere diameter. For $\alpha = 1$, η_α is obviously equal to the previously estimated structural stability threshold. As α decreases, η_α and, correspondingly, the stability range of the operator A_{mix} increase. Within the HNC equation this happens according to a roughly linear law, whereas at least a fourth-order polynomial is necessary in order to fit the PY data. The value assumed by η_α for $\alpha = 0$ cannot be computed directly since, in this case, the iterative cycle becomes the identity mapping $f_{n+1} = f_n$. However, the extrapolated values are, approximately, 0.665 for the HNC approximation and 0.8 for the PY equation.

The operator A has been interpreted as the mathematical counterpart of the physical process through which particle interactions build up correlations [1]. In this respect, one

may argue that A_{mix} corresponds to a process through which similar correlations are built up, although more slowly: the smaller α, the slower the process. Accordingly, it is tempting to interpret the resulting state of the system as an overcompressed, metastable state. The stability threshold of A_{mix} as $\alpha \rightarrow 0$ would then represent the highest density attainable by the fluid, no matter how slowly (carefully) the sample was prepared. Quite remarkably, the HNC result for hard spheres compares very well with the currently accepted value of the RCP packing fraction $\eta_{RCP} \simeq 0.64$ [6]. On the contrary, the PY estimate is even higher than the absolute close-packing fraction of hard spheres $\eta_{CP} = (\pi/6)\sqrt{2} \simeq 0.74$, corresponding to a face-centered cubic lattice. While keeping in mind that the above interpretation is not a rigorous one, this result

points once more to the greater reliability of the HNC equation and to the intrinsic limits of the PY approximation.

We conclude this note with a comment. If no special care is taken in order to "neutralize" the presence, at high densities, of the solid phase (e.g., by slowing down the process as is done when estimating η_{RCP}), the fluid runs into the structural stability threshold η_{inst}. This suggests that the thermodynamical stability boundary is somehow mirrored in the structural rearrangement of the fluid as the density approaches η_{inst}. It is then reasonable to hypothesize that a strong, though subtle, correlation exists between structural and thermodynamical stability.

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