On the bifurcation analysis of the liquid–solid instability in hard-sphere systems

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Recent bifurcation analyses of the BBGKY hierarchy for hard-sphere systems are shown to be equivalent to Kirkwood's linear response analysis. They suffer, therefore, from the same inconsistency which has been pointed out by Kunkin and Frisch. The decoupling scheme used also leads to an inconsistency in the stability analysis of the dynamic BBGKY hierarchy.

The question whether a hard-sphere fluid could develop an instability which indicates the transition to an ordered solidlike phase has been the subject of controversial discussions since the first theoretical approach given by Kirkwood.[1] In this note, we would like to comment on the origin of the discrepancy between the various theoretical predictions. We will restrict ourselves to the pure hard-core system, not including attractive forces between particles, since the theories for the latter models have been criticized recently by Sjölander and Turski.[2]

A linear response treatment by Kirkwood[1] indicated the instability of the fluid phase at a critical density ρ_c with respect to fluctuations in the density near a wavenumber $k_0 = 2\pi/a$, where "a" is the average particle spacing. Kunkin and Frisch[3] (KF) have argued that this instability appears due to an inconsistent linearization of the pair distribution function

$$g_2(\mathbf{r}_1, \mathbf{r}_2) \equiv \rho_2(\mathbf{r}_1, \mathbf{r}_2)/\rho_1(\mathbf{r}_1)\rho_1(\mathbf{r}_2) , \tag{1}$$

where $\rho_1(r_1)$ and $\rho_2(r_1, r_2)$ are the singlet and pair correlation functions, respectively.

Recent investigations by Raveché and Stuart (RS),[4,5] Yoshida and Kudo,[6] and Raveché and Kayser[7] on the BBGKY hierarchy use a bifurcation analysis, which produces an instability in close analogy to Kirkwood's results. Alternative analyses of the hard-core system use a different hierarchy and different closure. Specifically, Lovett[8] uses the "direct" correlation function $c(r_1, r_2)$ rather than the pair correlation function [Eq. (1)], and Weeks, Rice, and Kozak[9] use the Kirkwood–Salsburg integral equation. In these cases, there is no indication for a bifurcation associated with an instability in the hard-core systems.

In order to shed some light on this discrepancy, we start by concisely repeating KF's argument against the existence of an instability and then discuss the relation to the bifurcation analysis.

The first equation of the BBGKY hierarchy can be written, including an external potential $V_0(r_1)$, as

$$\nabla_1 \ln\rho_1(\mathbf{r}_1) = -\beta \int_\Omega \nabla_1 U(|\mathbf{r}_{12}|) \times g_2(\mathbf{r}_1, \mathbf{r}_2)\rho_1(\mathbf{r}_2)\, d\mathbf{r}_2 + \nabla_1 V_0(\mathbf{r}_1) , \tag{2}$$

where $U(|\mathbf{r}_{12}|)$ is the interparticle potential depending on the distance between pairs only. β is the inverse temperature, and the other functions are defined by Eq. (1). There are N particles in the volume Ω. The functions $\rho_1(\mathbf{r}_1)$ and $g_2(\mathbf{r}_1, \mathbf{r}_2)$ may be expressed, respectively, as

$$\rho_1(\mathbf{r}_1) = \rho_l[1 + \phi_1(\mathbf{r}_1)] , \tag{3a}$$

$$g_2(\mathbf{r}_1, \mathbf{r}_2) = g_2^l(\mathbf{r}_{12}) + \chi(\mathbf{r}_1, \mathbf{r}_2) , \tag{3b}$$

where ρ_l is the homogeneous density of the fluid and $g_2^l(\mathbf{r}_{12})$ is the corresponding fluid pair distribution. Equation (2) may be linearized as

$$-\beta^{-1}\nabla_1\phi_1(r_1) = \nabla_1 V_0(\mathbf{r}_1) + \rho_l \int_\Omega \nabla_1 \times U(|\mathbf{r}_{12}|)[g_2^l(\mathbf{r}_{12})\phi_1(\mathbf{r}_2) + \chi(\mathbf{r}_1, \mathbf{r}_2)]\, d\mathbf{r}_2 . \tag{4}$$

Fourier transforming this equation

$$\hat{\phi}_1(\mathbf{k}) = \int \phi(\mathbf{r}_1) \exp(-i\mathbf{k}\cdot\mathbf{r}_1)\, d\mathbf{r}_1 , \tag{5}$$

one obtains as solution

$$\hat{\phi}_1(\mathbf{k}) = M(\mathbf{k})/\{1 - G(\mathbf{k})\} , \tag{6}$$

with

$$M(\mathbf{k}) = \frac{i}{k^2} \int \mathbf{k}\cdot R(\mathbf{r}_1) \exp(-i\mathbf{k}\cdot\mathbf{r}_1)\, d\mathbf{r}_1 , \tag{7a}$$

$$R(\mathbf{r}_1) = \beta\nabla_1 V_0(\mathbf{r}_1) + \beta\rho_l \int d\mathbf{r}_2 \nabla_1 U(r_{12})\chi(\mathbf{r}_1, \mathbf{r}_2) , \tag{7b}$$

and

$$G(\mathbf{k}) = \frac{i}{k^2}\, \beta\rho_l \int \frac{\mathbf{k}\mathbf{r}}{|\mathbf{r}|}\, g_2^l(\mathbf{r})\, \frac{d}{d|r|}\, U(|r|) \exp(-i\mathbf{k}\cdot\mathbf{r})\, d\mathbf{r} . \tag{8}$$

This is Kirkwood's[1] equation, which he assumed to produce a singularity [Eq. (6)] at

$$G(\mathbf{k}) = 1 . \tag{9}$$

The expression for $G(\mathbf{k})$ in ν dimensions is given in the Appendix. However, KF[3] have noted that $\chi(\mathbf{r}_1, \mathbf{r}_2)$ contains a term which identically cancels the term $G(\mathbf{k})$ in Eq. (6) by going to the next equation in the hierarchy. Their conclusion, that there is no singularity in Eqs. (6)–(8), is not complete because of the possible occurrence of a singularity in χ. However, if there is a singularity in this set, it would then require the solution of the second equation of the hierarchy also.

The analogy between the linear response approach and the bifurcation analysis is obvious. Assume a macroscopic observable to be given [e.g., $A \equiv \rho_1(\mathbf{r})$] by a homogeneous nonlinear equation

$$A = Q\{A\} , \tag{10}$$

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where Q is a nonlinear operator, and the equation to have a basic solution A_0. A small externally applied potential F produces a small change of A_0 to A_0+a, which is in linear response

$$a=|1-Q'\{A_0\}|^{-1}F(A_0) , \tag{11}$$

with $Q'\{A_0\}=(\delta Q\{A\}/\delta A)$ at $A=A_0$. The response a diverges for the determinant

$$\det|1-Q'\{A_0\}|=0 , \tag{12}$$

with $F(A_0)\neq 0$. This corresponds to the singularity produced by Eq. (9). The bifurcation analysis is equivalent to condition (12), only the problem is cast into an eigenvalue problem

$$[1-Q'\{A_0\}]a=0 . \tag{13}$$

(Note that, since Q is an operator, $Q'\{A_0\}$ is a linear operator acting on a.) Nontrivial solutions to Eq. (13) require Eq. (12) to be fulfilled. These bifurcation treatments, therefore, are subject to the same criticism as pointed out by KF[3] for the Kirkwood[1] instability. In other words, they are incomplete because they do not consistently include both linearizations Eqs. (3a) and (3b) of the functions entering Eq. (2).

The procedure used by KF[3] is to simultaneously treat the second equation of the BBGKY hierarchy. However, it is of course possible to perform a consistent truncation directly after the first equation [Eq. (2)]. Such a truncation requires a self-consistent definition of the distribution $g_2(\mathbf{r}_1,\mathbf{r}_2)$ depending only upon $\rho_1(r)$ and U. Such a representation is provided by the Ornstein–Zernike relation, which relates the pair correlation $g_2(r_{12})$ to the direct correlation function $c(r_{12})$:

$$\hat{\Gamma}(k)\equiv\int[g_2(r)-1]\exp(-i\mathbf{k}\cdot\mathbf{r})\,d\mathbf{r} , \tag{17a}$$

$$\hat{c}(k)\equiv\int c(r)\exp(-i\mathbf{k}\cdot\mathbf{r})\,d\mathbf{r} , \tag{17b}$$

$$\hat{\Gamma}(k)\equiv\frac{\hat{c}(k)}{1-\rho_l\hat{c}(k)} . \tag{17c}$$

The structure function or static susceptibility $S(k)$ is given by

$$S(k)=1+\rho_l\hat{\Gamma}(k)=\frac{1}{1-\rho_l\hat{c}(k)} . \tag{18}$$

The direct correlation $c(r)$ in this zeroth order approximation (truncation after the first BBGKY equation) only depends upon the density ρ_l and the interaction potential. For a hard sphere system, $c(r)$ is negative if $|r|<d$ and zero if $|r|>d$. The expressions given in Ref. 8 are exact in one dimension and obtained from the Percus–Yevick approximation[10] in higher dimensions.

It is now possible in principle to evaluate Eqs. (2)–(8) in a self-consistent manner. However, there is an equivalent and mathematically simpler way. From formal linear response analysis, it is immediately clear that $\hat{\phi}_1(k)$ [Eq. (5)] is singular where $S(k)$ has a singularity. It is therefore sufficient to analyze Eq. (18) in order to investigate the stability of the hard-sphere system. This was done by Lovett[9] using the Percus–Yevick approximation for $c(r)$. No singularity was found in one and three dimensions for $S(k)$. This analysis also agrees with the exact result[11] that there is no transition in the one-dimensional system, in contrast to the analysis by Refs. 1 and 4–7.

We finally note that even more severe problems arise by using this inconsistent decoupling for dynamics, which was done by Kobayashi.[12] We summarize his treatment in the Appendix. For small k, $G(k)$ is negative and so is s, as it should be for the stable phase.[12] Applying this formalism to the hard-sphere system in three dimensions, one finds the following dispersion relation for $s/k\ll 1$ ($s\equiv i\omega$):

$$\frac{s}{k}\simeq\frac{-[1-G(k)]}{\sqrt{\pi}\,G(k)} . \tag{19}$$

Using $G(k)$ from Eq. (8), one obtains ($\nu=3$)

$$G(k)=\frac{-4\pi\rho d^3 g_2(d)}{(kd)^3}(\sin kd-kd\cos kd) , \tag{20}$$

where "bifurcation" occurs at $G(k)=1$. However, near the bifurcation point [Eq. (9)], s/k is positive. The system therefore has become unstable already at a density lower than the bifurcation density, while beyond the bifurcation point the fluid phase would be stable again. This clearly does not make sense and adds additional weight to our conclusion and the conclusion of other researchers[3,6,8] that the theory of freezing based on a decoupling of the first equation of the BBGKY hierarchy is not consistent with physical phenomena. Finally, we remark that at present there is no indication for the existence of such an instability of the hard-sphere fluid.

APPENDIX

The first equation of the dynamic BBGKY hierarchy is written as

$$\frac{\partial\rho_1}{\partial t}(\mathbf{r},\mathbf{p},t)=-\frac{\mathbf{p}}{m}\cdot\nabla_r\rho_1(\mathbf{r},\mathbf{p},t)-\int d\mathbf{r}'\int d\mathbf{p}'$$
$$\times\nabla_{r'}U(\mathbf{r}-\mathbf{r}')\rho_2(\mathbf{r};\mathbf{r}';\mathbf{p}\mathbf{p}',t)\cdot\nabla_p\rho(\mathbf{r},\mathbf{p},t) \tag{A1}$$

when hard-core interactions for $U(r)$ are assumed, ρ_2 is decoupled such that

$$\rho_2(\mathbf{r}\mathbf{r}',\mathbf{p},\mathbf{p}',t)=\rho_1(\mathbf{r},\mathbf{p},t)\rho_1(\mathbf{r}',\mathbf{p}',t)g_2(|\mathbf{r}-\mathbf{r}'|) , \tag{A2}$$

and Eq. (A1) is linearized about the fluid solution

$$\rho_1(\mathbf{r},\mathbf{p},t)=\rho_l f(\mathbf{p})[1+h(\mathbf{r},\mathbf{p},t)] , \tag{A3}$$

where

$$f(\mathbf{p})=(2\pi m)^{-\nu/2}\exp(-|\mathbf{p}|^2/2m) \tag{A4}$$

in ν dimensions. Then, we have

$$\frac{\partial h}{\partial t}=-\frac{\mathbf{p}}{m}\cdot\nabla_r h-\frac{\mathbf{p}}{m}\int d\mathbf{p}'$$
$$\times\int d\mathbf{r}'\,\nabla_r U(\mathbf{r}-\mathbf{r}')\rho_l g_2(|r-r'|)\,h(\mathbf{r}',\mathbf{p}',t)f(\mathbf{p}') ; \tag{A5}$$

this may be solved by the usual method of Fourier–Laplace transformation. The solution for

$$\hat{\phi}_1(\mathbf{k},s)=\int d\mathbf{p}f(\mathbf{p})h(\mathbf{k},\mathbf{p},s) \tag{A6}$$

is given by

$$\hat{\phi}_1(\mathbf{k}, s) = \frac{\int h(\mathbf{k}, \mathbf{p}, 0) f(\mathbf{p})\, d\mathbf{p}}{1 - G(k)\left[1 - s\int \frac{d\mathbf{p} f(\mathbf{p})}{\left(s + i\mathbf{k}\cdot\frac{\mathbf{p}}{m}\right)}\right]}, \qquad \text{(A7)}$$

where $G(k)$ is the same quantity defined in Eq. (8) and in ν dimensions it is

$$G(\mathbf{k}) = -\rho_l d^\nu \frac{g_2(d)}{kd} \frac{(2\pi)^\nu J_{\nu/2}(kd)}{2^{\nu-1}\pi^{\nu/2}} \left(\frac{2}{kd}\right)^{(\nu-2)/2}. \qquad \text{(A8)}$$

$J_{\nu/2}(kd)$ is a Bessel function of order $(\nu/2)$.

The zeroes of the denominator for $\phi_1(\mathbf{k}, s)$ reveal the stability of the perturbations about the constant solution.

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