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Nonexistence of Kirkwood's Instability in a Uniform Fluid

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Kirkwood's instability in the theory of fluid–solid transitions is proved to be impossible. Fluctuation of the one-particle distribution function in the first equation of the BGY hierarchy is investigated beyond Kunkin and Frisch's treatment. The second equation of the BGY hierarchy is utilized to eliminate the three-particle distribution function left in the Kunkin–Frisch result. The final expression for the first-order fluctuation of the one-particle distribution function under the presence of an external field is written in a form including only the pair correlation function and agrees identically with the one obtained from the direct expansion of the one-particle distribution function in terms of the external field.

KEY WORDS: Equilibrium statistical mechanics; theory of liquids; integral equation formalism.

1. INTRODUCTION

The fluid–solid transition in a classical system of hard-core particles is one of the important problems in statistical mechanics. In 1951, with use of the linearized Born–Green–Yvon (BGY) integral equation,[(1)] it was predicted by Kirkwood[(2)] that in some region of the density–temperature plane the one-particle distribution function is unstable with respect to small perturbations. An interesting aspect of Kirkwood's theory is that the instability occurs even when the pair correlation function has no singularity. It involves,

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however, some unreasonable results in the light of other relevant studies.[3,5] For example, his calculation yields an instability even in the hard-rod system,[5] which contradicts van Hove's rigorous result[4] that there is no phase transition in the hard-rod system.

The above discrepancy is, as has been pointed out by some authors,[3,5] attributed to Kirkwood's treatment of the fluctuations of the one-particle distribution function and the pair correlation function as independent of each other. Kunkin and Frisch[5] assumed that the fluctuations of the pair correlation function as well as of the one-particle distribution function are induced by an external field and calculated the fluctuations to the first order in the external field. Substituting the results into the BGY equation and retaining only the first-order terms, they showed that the kernel which leads to Kirkwood's instability is canceled by a term arising from the fluctuation of the pair correlation function.[3]

In Kunkin and Frisch's result, however, the fluctuation of the one-particle distribution function is expressed in terms of an equation including the three-particle distribution function and another type of instability is not entirely ruled out.

In this paper, we will demonstrate in a rigorous manner that the three-particle distribution function is eliminated and that the first-order fluctuation of the one-particle distribution function obtained from the linearized BGY equation is described only in terms of the pair correlation function. In the course of the calculation the second equation of the BGY hierarchy is invoked and full use is made of the functional derivative technique. It follows that the one-particle distribution function has no instability unless the pair correlation function has a singularity.

2. FORMULATION

We start with the first equation of the BGY hierarchy[1]

$$\nabla_1 \ln n_1(1) + \beta \nabla_1 U(1) = -\beta \int [\nabla_1 V(|1 - 2|)] n_1(2) g_2(1, 2)\, d2 \qquad (1)$$

where β is the inverse temperature, n_1 the one-particle distribution function, U the external potential, g_2 the pair correlation function, and V the pairwise interaction with spherical symmetry. The abbreviated notation i is used for the coordinate $\mathbf{r}_i$ of the particle i.

In a uniform fluid phase, the one-particle distribution function n_1 is constant and is equal to the density n. Suppose an infinitesimal external field $\epsilon u(1)$ is applied to the system and n_1 is modified as $n_1(1) = n(1 + \epsilon\phi(1))$. We

[3] It is also shown in Ref. 5 that in some cases the external perturbation often leads to a mechanically more stable system.

expand both sides of (1) in ϵ, employing a slightly different method from Kunkin and Frisch's, and retain the terms in the first order in ϵ. Noting that the pair correlation function g_2 is a functional of n_1,[6] we obtain

$$\nabla_1\phi(1) + \beta\,\nabla_1 U(1) = -\beta\int [\nabla_1 V(|1-2|)]\Gamma(1,2,3)n\phi(3)\,d3\,d2 \qquad (2)$$

with

$$\Gamma(1,2,3) = \left.\frac{\delta[n_1(2)g_2(1,2)]}{\delta n_1(3)}\right|_{U=0} = \int \left.\frac{\delta[n_1(2)g_2(1,2)]}{\delta e^{-\beta U(4)}}\right|_{U=0} \left.\frac{\delta e^{-\beta U(4)}}{\delta n_1(3)}\right|_{U=0} d4 \qquad (3)$$

In order to evaluate Γ, it is convenient to utilize the following identities.[7] The first is the functional derivative of the Ursell function with respect to $e^{-\beta U(1)}$.

The s-particle Ursell function $\mathscr{F}_s$ is defined by the recursion formula

$$\frac{\delta\left\{\left[\exp\sum_{i=1}^{s}\beta U(i)\right]\mathscr{F}_s(1,2,\ldots,s)\right\}}{\delta\{\exp[-\beta U(s+1)]\}} = \left[\exp\sum_{i=1}^{s+1}\beta U(i)\right]\mathscr{F}_{s+1}(1,2,\ldots,s,s+1) \qquad (4)$$

for $s \geqslant 1$ and

$$\mathscr{F}_1(1) \equiv n_1(1) = \frac{\delta \ln \Xi}{\delta e^{-\beta U(1)}}\, e^{-\beta U(1)}$$

where Ξ is the grand partition function. They can be related to the ordinary correlation functions as

$$\mathscr{F}_2(1,2) = n_1(1)n_1(2)[g_2(1,2) - 1] \qquad (5)$$

$$\mathscr{F}_3(1,2,3) = n_1(1)n_1(2)n_1(3)[g_3(1,2,3) - g_2(1,2) - g_2(2,3) - g_2(1,3) + 2] \qquad (6)$$

etc. For later use, we write down the first two equations of (4):

$$\frac{\delta\mathscr{F}_1(1)}{\delta e^{-\beta U(2)}} = e^{\beta U(2)}[\mathscr{F}_2(1,2) + \delta(1-2)\mathscr{F}_1(1)] \qquad (7)$$

$$\frac{\delta\mathscr{F}_2(1,2)}{\delta e^{-\beta U(3)}} = e^{\beta U(3)}\{\mathscr{F}_3(1,2,3) + [\delta(1-3) + \delta(2-3)]\mathscr{F}_2(1,2)\} \qquad (8)$$

where $\delta(1-2)$ is the Dirac delta function. The second useful identity is

$$\frac{\delta(-\beta U(1))}{\delta n_1(2)} = \frac{1}{n_1(2)}\,\delta(1-2) - C_2(1,2) \qquad (9)$$

where C_2 is the direct correlation function which is related to g_2 as

$$g_2(1, 2) - 1 = C_2(1, 2) + \int C_2(1, 3) n_1(3)[g_2(3, 2) - 1]\, d3 \qquad (10)$$

Here we substitute (7)–(9) into (3) and replace the Ursell functions by the ordinary correlation functions with the aid of (5) and (6). Then we find

$$\Gamma(1, 2, 3) = \delta(2 - 3) g_l(|1 - 2|) - n g_l(|1 - 2|) C_2{}^0(|2 - 3|) + n g_3{}^0(1, 2, 3) - n^2 \int g_3{}^0(1, 2, 4) C_2{}^0(|4 - 3|)\, d4 \qquad (11)$$

where g_l is the unperturbed radial distribution function. The superscript zero is also used to indicate the quantity in the unperturbed uniform fluid. Note that the quantities with the superscript zero have translational symmetry. In writing the result (11), we have discarded beforehand those terms which will vanish on integration on the rhs of (2) due to inversion symmetry.

After inserting (11) in (2), we take the Fourier transform of (2) to obtain

$$\tilde{\phi}(\mathbf{k}) + \beta \tilde{U}(\mathbf{k}) = \tilde{\phi}(\mathbf{k})[G(\mathbf{k}) - nG(\mathbf{k})\tilde{C}(\mathbf{k}) + nT(\mathbf{k}) - n^2 T(\mathbf{k})\tilde{C}(\mathbf{k})] = \tilde{\phi}(\mathbf{k}) \frac{G(\mathbf{k}) + nT(\mathbf{k})}{1 + n\tilde{h}(\mathbf{k})} \qquad (12)$$

where we have used the Fourier transforms defined by

$$\tilde{\phi}(\mathbf{k}) = \int \phi(\mathbf{r}) \exp(i\mathbf{k}\cdot\mathbf{r})\, d\mathbf{r} \qquad (13)$$

$$\tilde{U}(\mathbf{k}) = \int U(\mathbf{r}) \exp(i\mathbf{k}\cdot\mathbf{r})\, d\mathbf{r} \qquad (14)$$

$$\tilde{h}(\mathbf{k}) = \int [g_l(r) - 1] \exp(i\mathbf{k}\cdot\mathbf{r})\, d\mathbf{r} \qquad (15)$$

$$G(\mathbf{k}) = -\frac{in\beta}{\mathbf{k}^2} \int \frac{\mathbf{k}\cdot\mathbf{r}}{r} \frac{dV(r)}{dr} g_l(r) \exp(i\mathbf{k}\cdot\mathbf{r})\, d\mathbf{r} \qquad (16)$$

$$\tilde{C}(\mathbf{k}) = \int C_2{}^0(r) \exp(i\mathbf{k}\cdot\mathbf{r})\, d\mathbf{r} = \frac{\tilde{h}(\mathbf{k})}{1 + n\tilde{h}(\mathbf{k})} \qquad (17)$$

and

$$T(\mathbf{k}) = -\frac{in\beta}{\mathbf{k}^2} \int \frac{\mathbf{k}\cdot\mathbf{R}_{12}}{R_{12}} \frac{dV(R_{12})}{dR_{12}} g_3{}^0(\mathbf{R}_{13}, \mathbf{R}_{23}) \exp(i\mathbf{k}\cdot\mathbf{R}_{13})\, d\mathbf{R}_1\, d\mathbf{R}_2 = -\frac{in\beta}{\mathbf{k}^2} \int \frac{\mathbf{k}\cdot(\mathbf{X} - \mathbf{Y})}{|\mathbf{X} - \mathbf{Y}|} \left.\frac{dV(R)}{dR}\right|_{R = |\mathbf{X} - \mathbf{Y}|} g_3{}^0(\mathbf{X}, \mathbf{Y}) \exp(i\mathbf{k}\cdot\mathbf{X})\, d\mathbf{X}\, d\mathbf{Y} \qquad (18)$$

It is important to note that the three-particle distribution function can be eliminated from $T(\mathbf{k})$. To show this, we employ the second equation of the

BGY hierarchy for the uniform fluid,[1]

$$\begin{aligned}\nabla_1 g_l(|1-2|) + \beta g_l(|1-2|)\,\nabla_1 V(|1-2|) &= -n\beta \int [\nabla_1 V(|1-3|)] g_3{}^0(1,2,3)\,d3 \\ &= -n\beta \int [\nabla_1 V(|1-3|)] g_3{}^0(1-2, 3-2)\,d3 \end{aligned} \tag{19}$$

The Fourier transform of (19) yields an important result:

$$T(\mathbf{k}) = \tilde{h}(\mathbf{k}) - (1/n)G(\mathbf{k}) \tag{20}$$

On substituting (20) into (13), we finally obtain

$$\tilde{\phi}(\mathbf{k}) = -\beta \tilde{U}(\mathbf{k})[1 + n\tilde{h}(\mathbf{k})] \tag{21}$$

The same result can be derived by expanding $n_1(1)$ directly with respect to $\epsilon u(1)$:

$$\epsilon n\phi(1) = \int \frac{\delta n_1(1)}{\delta e^{-\beta U(2)}}\bigg|_{u=0} [-\beta\epsilon U(2)]\,d2 \tag{22}$$

With the aid of (5) and (7), it can be easily shown that the Fourier transform of (22) agrees with (21). It implies that no instability can occur in the one-particle distribution function in the uniform fluid phase unless $h(\mathbf{k})$ has a singularity.

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