This article was downloaded by: On: 28 January 2011 Access details: Access Details: Free Access Publisher Taylor & Francis Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37- 41 Mortimer Street, London W1T 3JH, UK

Physics and Chemistry of Liquids

Publication details, including instructions for authors and subscription information: <http://www.informaworld.com/smpp/title~content=t713646857>

Relation Between Direct and Total Three-Body Correlations

G. Senatore^{ab}; N. H. March^e ^a Physics Department, University of Kentucky, Lexington, KY, USA ^b Dipartimento di Fisica Teorica, Universita' di Trieste, Trieste, Italy ^c Theoretical Chemistry Department, University of Oxford, Oxford, U.K.

To cite this Article Senatore, G. and March, N. H.(1986) 'Relation Between Direct and Total Three-Body Correlations', Physics and Chemistry of Liquids, 16: 2, $131 - 135$

To link to this Article: DOI: 10.1080/00319108608078510 URL: <http://dx.doi.org/10.1080/00319108608078510>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use:<http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Phys. Chem. Liy., 1986,Vol. 16, pp. 131-136 (C] **1986** Gordon and Breach Science Publishers, Inc. Printed in the United Kingdom 0031-9104/86/1602-0131\$18.50/0

Relation Between Direct and Total Three- Body Correlations

G. SENATORE?

Physics Department, University of Kentucky, Lexington KY 40506. USA.

and

N. H. MARCH

Theoretical Chemistry Department, University of Oxford. 1 South Parks Rd., Oxford OX1 3TG. U.K.

(Received May 13, 1986)

Recent work of Hernando prompts **us** to give simple derivations of relations between three-body direct and total correlation functions. These relations are then discussed in relation to the decomposition of the Ornstein-Zernike two body function $c(r)$ into 'potential' and 'cooperative' parts. Illustrations are referred to for the two-dimensional plasma and for critical point behaviour.

1 INTRODUCTION

The purpose of the present note is: (i) To give simple derivations of relations between three-body direct and total correlation functions, $c^{(3)}$ and $g^{(3)}$ respectively, prompted by Hernando's recent diagrammatic analysis.¹ (ii) To relate this to our recent discussion² of the division of the Ornstein-Zernike two-body correlation function *c(r)* into the sum of a 'potential' part $c_n(r)$ and a 'cooperative' part $c_n(r)$. (iii) To display the relation of the decoupling scheme of Ichimaru³ to Hernando's **work.**

t On leave from Dipartimento di Fisica Teorica, Universita' di Trieste, Trieste, Italy.

2 LIQUID STRUCTURE IN AN EXTERNAL POTENTIAL

We begin by studying the statistical mechanics of a liquid in the presence of an external potential V . Introducing the dimensionless quantity

$$
v = -V/K_B T \equiv -\beta V, \tag{1}
$$

we can write

$$
\frac{\delta v(1)}{\delta n(2)} = -\hat{c}(12) = -\left[c(12) - \frac{\delta(12)}{n(1)}\right]
$$
 (2)

with $n(1)$ the single-particle density and $c(12) \equiv c(\mathbf{r}_1, \mathbf{r}_2)$. The threebody direct correlation function $c^{(3)} \equiv c(123)$ is now given in terms of $\hat{c}(12)$ by $\frac{\partial}{\partial n(2)} = -\hat{c}(12) = -\left[c(12) - \frac{\hat{c}(12)}{n(1)} \right]$ (2)

ingle-particle density and $c(12) = c(\mathbf{r}_1, \mathbf{r}_2)$. The three-

relation function $c^{(3)} \equiv c(123)$ is now given in terms of
 $c(123) = \frac{\delta c(12)}{\delta n(3)} = \frac{\delta \hat{c}(12)}{\$

$$
c(123) = \frac{\delta c(12)}{\delta n(3)} = \frac{\delta \hat{c}(12)}{\delta n(3)} - \frac{\delta (12)\delta (13)}{n(1)^2}.
$$
 (3)

Furthermore we can write

$$
\frac{\delta n(1)}{\delta v(2)} = \hat{n}(12) = n(12) - n(1)n(2) + n(1)\delta(12)
$$

= $n(1)n(2)h(12) + n(1)\delta(12)$ (4)

with $n(12)$ the two-point density and $h(12) = g(12) - 1$, where $g(12)$ is the usual liquid pair function. From Eq. (4) we find

$$
\frac{\delta \hat{n}(12)}{\delta v(3)} = \hat{n}(123) = n(123) - n(12)n(3) + n(12)[\delta(13) + \delta(23)]
$$

\n
$$
- n(1)\hat{n}(23) - n(2)\hat{n}(13) + \hat{n}(13)\delta(12)
$$

\n
$$
= n(1)n(2)n(3)h(123) + \hat{n}(12)\delta(23) + \hat{n}(13)\delta(12)
$$

\n
$$
+ \hat{n}(23)\delta(13) - n(1)[\delta(13)\delta(12) + \delta(23)\delta(12)].
$$
 (5)

Next we have the Ornstein-Zernike relation

$$
\int d4 \frac{\delta n(1)}{\delta v(4)} \frac{\delta v(4)}{\delta n(2)} = \delta(12) = -\int d4 \hat{n}(14) \hat{c}(42) \tag{6}
$$

and taking its functional derivative with respect to $n(3)$ yields:

$$
0 = \int d4 \frac{\delta \hat{n}(14)}{\delta n(3)} \hat{c}(42) + \int d4 \hat{n}(14) \frac{\delta \hat{c}(42)}{\delta n(3)}.
$$
 (7)

If we now apply $\int d\theta$ $\hat{c}(1', 1)$ or $\int d\theta$ $\hat{n}(2, 2')$ we obtain

$$
\frac{\delta \hat{c}(12)}{\delta n(3)} = \int d4 \int d5 \, \hat{c}(15) \, \frac{\delta \hat{n}(54)}{\delta n(3)} \, \hat{c}(42) \tag{8}
$$

or

$$
\frac{\delta \hat{n}(12)}{\delta n(3)} = \int d4 \int d5 \hat{n}(14) \frac{\delta \hat{c}(45)}{\delta n(3)} \hat{n}(52). \tag{9}
$$

Equation (8) derived above by functional differentiation is fully equivalent to Hernando's Eq. (41), which is readily obtained by utilizing the identity

$$
\frac{\delta \hat{n}(54)}{\delta n(3)} = \int d6 \frac{\delta \hat{n}(54)}{\delta v(6)} \frac{\delta v(6)}{\delta n(3)} = -\int d6 \hat{n}(546) \hat{c}(63). \tag{10}
$$

By considering $\int d3$ of Eq. (8) or (9) one obtains relations which express $\partial c(12)/\partial n$ in terms of $\partial n(12)/\partial n$ and $c(12)$ or $\partial n(12)/\partial n$ in terms of $\partial c(12)/\partial n$ and $n(12)$, after letting the external potential tend to zero.

Thus one finds

$$
\frac{\delta \hat{c}(12)}{\partial n} = \int d4 \int d5 \, \hat{c}(14) \, \frac{\partial \hat{n}(54)}{\partial n} \, \hat{c}(42) \tag{11}
$$

and

$$
\frac{\partial \hat{n}(12)}{\partial n} = \int d4 \int d5 \, \hat{n}(14) \, \frac{\partial \hat{c}(45)}{\partial n} \, \hat{n}(42). \tag{12}
$$

By using

$$
\frac{\partial \hat{c}(12)}{\partial n} = \frac{\partial c(12)}{\partial n} + \frac{\delta(12)}{n^2}
$$
 (13)

and

$$
\frac{\partial \hat{n}(12)}{\partial n} = \frac{\partial n(12)}{\partial n} - 2n + \delta(12) \tag{14}
$$

one finds, after a little algebra

$$
\frac{\partial c(12)}{\partial n} = -\int d3 c(13)c(32) + \frac{\partial g(12)}{\partial n} + 2n \int d3 c(13) \frac{\partial g(32)}{\partial n} + n^2 \int d3 \int d4 c(13)c(24) \frac{\partial g(34)}{\partial n}
$$
\n(15)

and

$$
\frac{\partial g(12)}{\partial n} = \int d3 h(13)h(32) + \frac{\partial c(12)}{\partial n} + \int d3 h(13) \frac{\partial c(32)}{\partial n} + n^2 \int d3 \int d4 h(13)h(24) \frac{\partial c(34)}{\partial n}.
$$
 (16)

3 RELATION TO DECOMPOSITION OF *e(r)*

One can insert the decomposition²

$$
c(r) = c_p(r) + c_c(r) \tag{17}
$$

into Eq. (16) and hence obtain an integral equation for ∂c , ∂n explicitly in terms of *g* and of the density derivatives of the quantities determining $c_p(r)$ namely,² ϕ , *g,* $\partial g/\partial r$ *,* $\partial g/\partial n$ *,* $\partial^2 g/\partial n\partial r$ *.* Alternatively, the various derivatives of *g* may be written in terms of *g* itself and three, four and five-body Ornstein-Zernike functions.

As in [2], one can make the above quite explicit on the twodimensional plasma, but though the example is illuminating in the present context it does not yield new results so we shall not give the details.

As a second example, we mention our own critical point work.⁴ One can insert into the integral involving $g^{(3)}$, which diverges at the critical point, the above relation between $g^{(3)}$ and $c^{(3)}$. But decoupling still seems to be necessary on $c^{(3)}$ to proceed beyond this point.

4 DECOUPLING OF THREE-BODY DIRECT CORRELATION FUNCTION

Finally, in the context of decoupling, the approximation

$$
c(123) = h(12)h(23)h(31)
$$
 (18)

is discussed by Hernando.¹ Since above we have related $q^{(3)}$ and $q^{(3)}$. we can rewrite the so-called force equation

$$
-\frac{\partial U(r_{12})}{\partial \mathbf{r}_1} = -\frac{\partial \phi(r_{12})}{\partial \mathbf{r}_1} - \int d\mathbf{r}_3 \frac{n(r_1, r_2, r_3)}{n^2 g(r_{12})} \frac{\partial \phi(r_{13})}{\partial \mathbf{r}_1}, \quad (19)
$$

where $g(r) = \exp[-U(r)/K_B T]$ defines the potential of mean-force and $\phi(r)$ is the two-body interparticle pair potential, solely in terms of $c^{(3)}$. Use of the decoupling (18) in the resulting equation does not lead to the Born-Green approximation⁵ of liquid structure theory, and presumably transcends it. It turns out,³ in fact, that Eq. (18) follows from a combination of convolution and Kirkwood superposition approximation.? However, one must not expect **Eq.** (18) to be sufficiently refined to work near the critical point.

t **This corrects a minor inaccuracy in the paper of Hernando [l]; all his major conclusions remain intact.**

References

- 1. **J. A.** Hernando, *Phys. Rev.,* A33, 1338 (1986).
- 2. R. I. M. A. Rashid, G. Senatore and N. **H.** March, *Phys. Chem. Liq.,* **16,** 1 (1986).
- 3. S. Ichimaru, *Reo.* Mod. *Phys., 54,* 1017 (1982).
- 4. G. Senatore and N. H. March, *J. Chem. Phys., 80,* 5242, (1984).
- 5. See, for example, N. H. March, Liquid metals (Pergamon: Oxford) 1968.