RAPID COMMUNICATIONS

PHYSICAL REVIEW A VOLUME 29, NUMBER 2 FEBRUARY 1984

Asymptotic behavior of three-particle correlations

H. J. Raveché and R. F. Kayser
Thermophysics Division, National Bureau of Standards, Washington, D.C. 20234
(Received 5 October 1983)

The three-particle correlation function $G_3(r_{12},r_{13},r_{23})$ for a fluid with a long-range pair potential is computed in two limits: (a) all $r_{ij} \rightarrow \infty$, and (b) one distance, say r_{12}, fixed and $r_{13},r_{23} \rightarrow \infty$. In both cases, the pair potential times the square of the isothermal compressibility appears.

A variety of studies on the triplet correlation function $G_3(r_{12},r_{13},r_{23})$ of a fluid have appeared recently, including work on critical-point properties,[1,2] integral equation theories,[3] and exact integral identities.[4] To model certain characteristics of fluids, consideration must be given to the fact that, in general, the interactions between particles in a real fluid cannot be set equal to zero beyond some arbitrarily chosen finite range.[5] The purpose of this Rapid Communication is to report the calculation of the asymptotic behavior of G_3 at large distances for a fluid with a long-range pair potential, $\phi(r)$. A familiar example of such an interaction is the induced dipole-induced dipole potential which varies as $\phi(r) \simeq -A/r^6$ provided retardation effects can be neglected (this being the case for distances less than a few hundred angstroms[6]). More generally, the term long-range interaction is used here to denote any non-finite-range pair potential that is integrable at infinity.

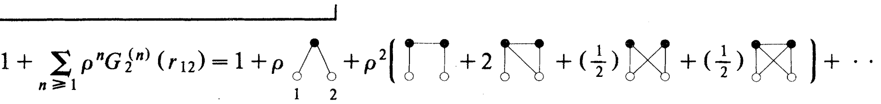
The present calculation is based on a resummation of the density expansion of the pair correlation function[7] $G_2(r)$ and of the triplet function.[8] As will be evident, this method for investigating the asymptotic behavior is simple, and extendable to higher-order correlation functions as well as to fluid mixtures. The calculation focuses on two limits of G_3: (a) all $r_{ij} \rightarrow \infty$ and (b) one distance, say r_{12}, fixed and $r_{13},r_{23} \rightarrow \infty$. The former is of interest as a comparison with $G_2(r)$, $r \rightarrow \infty$, for which it has been found[5,9,10] that

$$G_2(r) = 1 - (\rho\chi/\beta)^2 \beta\phi(r) \ , \tag{1}$$

where ρ is the number density, $\chi = \rho^{-1}(\partial\rho/\partial P)$ is the isothermal compressibility, P is the pressure, and β is $1/kT$ with k Boltzmann's constant and T the absolute temperature. The limit (b) is germane to the closure problem[1-4] in the theory of fluids and will be shown to lead to a correction to the superposition approximation of Kirkwood, which assumes that G_3 is a symmetrized product of three pair-correlation functions.

In the notation of Henderson,[8] the density expansions of the correlation functions are as follows:

$$\exp[\beta\phi(r_{12})]G_2(r_{12}) = 1 + \sum_{n \geq 1} \rho^n G_2^{(n)}(r_{12}) = 1 + \rho \ \ldots \tag{2}$$

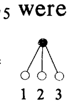


and

$$\exp\{\beta[\phi(r_{12})+\phi(r_{13})+\phi(r_{23})]\}G_3(r_{12},r_{13},r_{23}) = 1 + \sum_{n \geq 1} \rho^n \tau_n(r_{12},r_{13},r_{23})$$
$$= 1 + \rho[G_2^{(1)}(r_{12}) + G_2^{(1)}(r_{13}) + G_2^{(1)}(r_{23}) + \delta_4(r_{12},r_{13},r_{23})]$$
$$+ \rho^2\{G_2^{(1)}(r_{12})G_2^{(1)}(r_{13}) + G_2^{(1)}(r_{13})G_2^{(1)}(r_{23}) + G_2^{(1)}(r_{12})G_2^{(1)}(r_{23})$$
$$+ G_2^{(2)}(r_{12}) + G_2^{(2)}(r_{13}) + G_2^{(2)}(r_{23})$$
$$+ [G_2^{(1)}(r_{12}) + G_2^{(1)}(r_{13}) + G_2^{(1)}(r_{23})]\delta_4(r_{12},r_{13},r_{23})$$
$$+ \tfrac{1}{2}[\delta_4(r_{12},r_{13},r_{23})]^2 + \delta_5(r_{12},r_{13},r_{23})\} + \cdots \ . \tag{3}$$

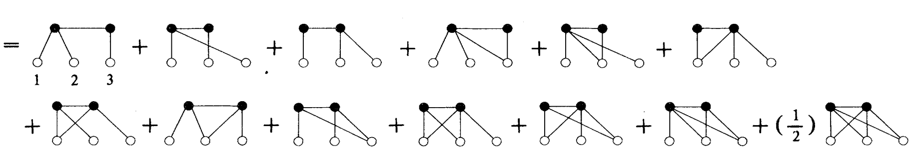
The graphs δ_4 and δ_5 were introduced by Salpeter[8] to represent

$$\delta_4(r_{12},r_{13},r_{23}) = \tag{4}$$



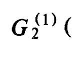
and

$$\delta_5(r_{12},r_{13},r_{23}) = \ldots \ . \tag{5}$$

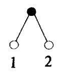
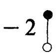


Standard notation prevails in Eqs. (2) through (5): Lines, which represent factors of $f(r_{ij}) = e^{-\beta\phi(r_{ij})} - 1$ between particles, connect open circles denoting fixed particle positions and/or solid circles (vertices) indicating integration over the position of a particle. Throughout the report open circles are numbered, in increasing order, from left to right.

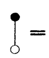
To ascertain how the graphs are analyzed consider

$G_2^{(1)}(r_{12}) =$  $= \int d\vec{r}_3 f(r_{13}) f(r_{23})$ (6)

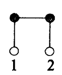
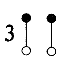
for $r_{12} \to \infty$. The integrand decays as $\phi(r_{12})$ when the particle at $\vec{r}_3$ is near either $\vec{r}_1$ or $\vec{r}_2$, but decays at least as fast as $[\phi(r_{12})]^2$ when $\vec{r}_3$ is far from both $\vec{r}_1$ and $\vec{r}_2$. The latter region of integration leads to higher-order contributions to (6) and these are neglected systematically in this study. Now when $\vec{r}_3$ is near $\vec{r}_1$, $f(r_{23})$ may be approximated by $-\beta\phi(r_{12})$, and similarly, when $\vec{r}_3$ is near $\vec{r}_2$, $f(r_{13})$ may also be approximated by $-\beta\phi(r_{12})$, giving

 $= -2$  $\beta\phi(r_{12})$, (7)

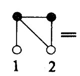
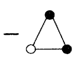
where

 $= \int d\vec{r}_2 f(r_{12})$.

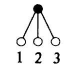
The analyses of the graphs in (2) with two vertices use the same reasoning, but those graphs where both $\vec{r}_1$ and $\vec{r}_2$ have more than one bond can be neglected since they decay at least as fast as $[\phi(r_{12})]^2$ in the limit $r_{12} \to \infty$. Thus the graphs which contribute to (2) in this limit are

 $= -3$  $\beta\phi(r_{12})$ (8a)

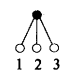
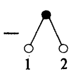
and

 $= -$  $\beta\phi(r_{12})$. (8b)

Turn next to the graphs in δ_4 and δ_5, and for illustrative purposes consider the integral representation of δ_4,

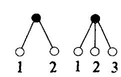
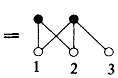
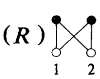
 $= \int d\vec{r}_4 f(r_{14}) f(r_{24}) f(r_{34})$, (9)

in limit (b), i.e., r_{12} fixed and $\vec{r}_3 \to \infty$. The integrand decays at least as fast as $[\phi(r_{12})]^2$ unless $\vec{r}_4$ remains near both $\vec{r}_1$ and $\vec{r}_2$, and in this region $f(r_{34})$ may be approximated either by $-\beta\phi(r_{13})$ or by $-\beta\phi(r_{23})$. If R is used as a measure of either r_{13} or r_{23}, then in limit (b) δ_4 reduces to

 $= -$  $\beta\phi(R)$. (10)

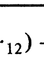
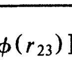
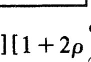
On the other hand, in limit (a) (where all $r_{ij} \to \infty$) δ_4 decays at least as fast as $[\phi(r_{ij})]^2$ since two bonds must be broken. Consequently this graph can be omitted in limit (a). The analysis of δ_5, which consists of graphs with two vertices, is facilitated by the following observations: (i) In limit (a) all graphs decay faster than $\phi(r_{ij})$ and can therefore be neglected; (ii) the graphs for which $\vec{r}_3$ has more than one bond do not contribute in limit (b) since they decay at least as fast as $[\phi(R)]^2$.

From (3) through (5) it is seen that two types of product graphs also appear: $G_2^{(1)}\delta_4$ and $(\delta_4)^2$. These are readily analyzed in limit (a) by noting from (7) and (10) that both product graphs can be neglected. For limit (b) the result (10) shows further that $(\delta_4)^2$ is negligible and for the remaining product graph in this limit one has

 $=$  $= -\beta\phi(R)$  , (11)

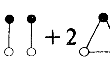
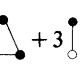
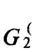
where $R \simeq r_{13} \simeq r_{23}$ is again a measure of the distance of $\vec{r}_3$ to either $\vec{r}_1$ or $\vec{r}_2$.

The graphical investigation outlined above can now be used to determine the form of G_3 at large interparticle distances. For the case where all $r_{ij} \to \infty$, one finds

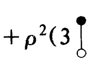
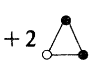
$G_3(r_{12}, r_{13}, r_{23}) = 1 - \beta[\phi(r_{12}) + \phi(r_{13}) + \phi(r_{23})][1 + 2\rho$  $+ \rho^2(3$  $+ 2$  $) + \cdots]$, (12)

whereas the graphs combine in limit (b) to give

$G_3(r_{12}, r_{13}, r_{23}) = G_2(r_{12}) - 2\beta\phi(R)\exp[-\beta\phi(r_{12})]\{1 + \rho[2$  $+ \frac{3}{2} G_2^{(1)}(r_{12})]$

$+ \rho^2[3$  $+ 2$  $+ 3$  $G_2^{(1)}(r_{12}) + 2G_2^{(2)}(r_{12})] + \cdots\}$. (13)

From the virial expansion of the pressure,[11] however, one finds

$(\rho\chi/\beta)^2 = 1 + 2\rho$  $+ \rho^2(3$  $+ 2$  $) + \cdots$, (14)

which when applied to (12) yields the resummation

$$G_3(r_{12}, r_{13}, r_{23}) = 1 - (\rho\chi/\beta)^2 \beta[\phi(r_{12}) + \phi(r_{13}) + \phi(r_{23})] \ . \tag{15}$$

The series at (13) may be similarly resummed by using (14) and the fact that

$$\rho^{-1}\partial\rho^2 G_2(r_{12})/\partial\rho = 2\exp[-\beta\phi(r_{12})][1 + \tfrac{3}{2}\rho G_2^{(1)}(r_{12}) + 2\rho^2 G_2^{(2)}(r_{12}) + \cdots] \ , \tag{16}$$

and for limit (b) this implies

$$G_3(r_{12}, r_{13}, r_{23}) = G_2(r_{12}) - \rho^{-1}[\partial\rho^2 G_2(r_{12})/\partial\rho](\rho\chi/\beta)^2 \beta\phi(R) \ . \tag{17}$$

The pair potential in both (15) and (17) can be eliminated by using (1) and this leads to expressions for the asymptotic form of G_3 in terms of $h(r)=G_2(r)-1$. In the case of limit (a) the expression is

$$G_3(r_{12},r_{13},r_{23})=1+h(r_{12})+h(r_{13})+h(r_{23}) \ , \qquad (18)$$

while limit (b) reduces to

$$G_3(r_{12},r_{13},r_{23})=G_2(r_{12})+\rho^{-1}[\partial\rho^2 G_2(r_{12})/\partial\rho]h(R) \ . \qquad (19)$$

The similarity between (1) and (18) suggests the following form for the n-particle correlation function in limit (a):

$$G_n(\vec{r}_1,\ldots,\vec{r}_n)=1-(\rho\chi/\beta)^2\beta\sum_{1\leq i<j\leq n}\phi(r_{ij})$$
$$=1+\sum_{1\leq i<j\leq n}h(r_{ij}) \ . \qquad (20)$$

The result (19) leads to a correction to the superposition approximation, i.e.,

$$G_3(r_{12},r_{13},r_{23})/G_2(r_{12})G_2(r_{13})G_2(r_{23})\simeq 1$$

of the form

$$G_3(r_{12},r_{13},r_{23})/G_2(r_{12})G_2(r_{13})G_2(r_{23})$$
$$=1+\rho[\partial\ln G_2(r_{12})/\partial\rho]h(R) \ . \qquad (21)$$

In summary, the asymptotic form of the three-particle correlation function at large distances for a fluid with a long-range pair potential has been calculated in two limits. An interesting feature of the decay of G_3 is the appearance of $(\rho\chi/\beta)^2$, which is near unity at low densities, much smaller than unity at high densities, and anomalously large near the critical point. The derivation given here rests on the assumptions of uniform convergence of (2) and (3) and convergence of (14). In general, little is known about the convergence of these series, and in particular it has not been shown that the radius of convergence is limited to low densities. Indeed, the results for the decay of G_3 appear to apply in their respective limits to any fluid state of finite compressibility. The particular result (19) is in fact supported by two independent studies. One of these[12] utilizes a Legendre-polynomial expansion for G_3 in conjunction with integral relations such as that for the density derivative of the pair correlation function. The other study[2] (see also Kuni in Ref. 9) is based on a functional expansion for the conditional probability of finding a particle at $\vec{r}_3$ given that there are particles at $\vec{r}_1$ and $\vec{r}_2$.

[1]G. L. Jones, Phys. Rev. Lett. 50, 2090 (1983).
[2]R. F. Kayser and H. J. Raveché, Phys. Rev. A 26, 2123 (1982).
[3]See, for example, A. D. J. Haymet, S. A. Rice, and W. G. Madden, J. Chem. Phys. 74, 3033 (1981); 75, 4696 (1981).
[4]B. U. Felderhof, Physica A 120, 103 (1983).
[5]G. Stell, Phys. Rev. 184, 135 (1969); G. Stell, in *Statistical Mechanics, Part A: Equilibrium Techniques,* edited by B. J. Berne (Plenum, New York, 1977), p. 47.
[6]J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1959), p. 967; G. C. Maitland, M. Rigby, E. Smith, and W. A. Wakeham, *Intermolecular Forces, Their Origin and Determination* (Clarendon, Oxford, 1981), p. 22.
[7]J. de Boer and A. Michels, Physica 6, 97 (1939); J. E. Mayer and E. Montroll, J. Chem. Phys. 9, 2 (1941).
[8]E. Meeron, J. Chem. Phys. 27, 1238 (1957); E. E. Salpeter, Ann. Phys. (N.Y.) 183 (1958); D. Henderson, J. Chem. Phys. 46, 4306 (1967).
[9]J. E. Enderby, T. Gaskell, and N. H. March, Proc. Phys. Soc. London 85, 217 (1965); F. M. Kuni, Dokl. Phys. Chem. 179, 153 (1968).
[10]R. F. Kayser and H. J. Raveché, Phys. Rev. A 29, 1013 (1984) (this issue).
[11]T. L. Hill *Statistical Mechanics* (McGraw-Hill, New York, 1956), Chap. 5.
[12]I. Z. Fisher, Zh. Eksp. Teor. Fiz. 63, 1548 (1972) [Sov. Phys. JETP 35, 811 (1972)].