

Systems with Weak Long-Range Potentials

P.C.Hemmer

Institutt for teoretisk fysikk, NTH,  
Universitetet i Trondheim, Norway

and

J.L.Lebowitz\*

Belfer Graduate School of Science,  
Yeshiva University, New York, New York, USA

## I. INTRODUCTION

### A. The van der Waals-Maxwell Theory.

The difficulties encountered in obtaining from theory, the properties of matter when the interactions between the atoms or molecules produce phase transitions, are well-known. Indeed the advance in our understanding of these phenomena since the time of van der Waals is probably not as great as our remaining ignorance. The reason for these difficulties is the complicated correlations between the particles induced by the interactions. It was a great achievement of van der Waals to realize that the universal existence of a gas-liquid phase transition at low temperatures, terminating at some critical temperature  $T_c$ , can be understood qualitatively as arising in a simple way from some general features of the interaction between molecules.\* To this end van der Waals (1873) visualized the interaction potential between a pair of molecules a distance  $r$  apart,  $u(r)$ , as consisting of two separate additive parts, a short-range repulsive part  $q(r)$  and a long-range attractive part  $w(r)$ ,

$$u(r) = q(r) + w(r) \quad (1.1)$$

The short-range part keeps the particles apart and is responsible for detailed correlations. The long-range part on the other hand sees only the gross, essentially macroscopic,

---

\*For a historical account of van der Waals' work see article by Brush (1970) and articles by de Boer (1974) and Klein (1974). The latter two were presented as lectures at the 1973 IUPAP Conference in Amsterdam celebrating the centennial of the van

(Fig.1)

For  $T > T_c$  the van der Waals equation of state gives a good qualitative representation of the isotherms of a real fluid; For  $T < T_c$ , however, each isotherm includes a section where the compressibility is negative, in violation of the thermodynamic stability principle. The primary reason for this failure is, as will become amply clear later, that the argument about the effect of the long-range potential  $w(r)$  being independent of the detailed correlations is only valid when the range of the correlations is small compared to the range of  $w(r)$ . This necessarily requires the system to be in a single phase; it does not allow for the possibility of coexisting liquid and vapour phases at different densities.

Maxwell (1875) showed that the coexistence region could be included in the theory by using the van der Waals equation of state for both liquid and vapour phases and using the thermodynamic equilibrium condition that the two phases must have equal pressures and chemical potentials. This leads to the following modification of (1.2) for  $T < T_c$  :

$$p = MC_1 p_{vdW}(\rho, T) = \begin{cases} p_{vdW}(\rho, T) & \text{if } \rho < \rho_v(T) \text{ or } \rho > \rho_l(T) \\ p_{sat}(T) & \text{if } \rho_v(T) < \rho < \rho_l(T) \end{cases} \quad (1.3)$$

where  $\rho_v(T)$ ,  $\rho_l(T)$  and  $p_{sat}(T)$  may be determined by the graphical construction shown in Fig.1.

concerned a one-dimensional system for which the short-range repulsive potential  $q(r)$  is infinite for  $r < d$  and vanishes for  $r > d$  (hard rods of diameter  $d$ ) and an attractive interaction  $w(r)$  which contained an inverse range parameter  $\gamma$

$$w(r, \gamma) = -a\gamma e^{-\gamma r} . \quad (1.4)$$

Using a formalism based on Wiener processes (Kac, 1959) especially adopted to this problem Kac, Uhlenbeck and Hemmer were able to prove rigorously the validity of the van der Waals equation of state (1.2) (with  $b$  replaced by  $d$ ), together with the Maxwell rule (1.3), in the van der Waals limit  $\gamma \rightarrow 0$ .

The limit process  $\gamma \rightarrow 0$ , provides a clear distinction between the short range of  $q(r)$  and the long (infinite as  $\gamma \rightarrow 0$ ) range of  $w(r, \gamma)$ . This limit was first used by Baker (1961) in his study of spin systems.

Lebowitz and Penrose (1966) combined the ideas of van Kampen with the use of the van der Waals limit  $\gamma \rightarrow 0$ . They considered systems with interparticle potentials of the form (1.1) with  $w(r)$  a Kac potential of the form

$$w(\underline{r}, \gamma) = \gamma^\nu \varphi(\gamma \underline{r}) , \quad (1.5)$$

where  $\nu$  is the dimensionality of the space considered. This reduces to (1.4) when  $\nu = 1$  and  $\varphi(x) = -a e^{-x}$ . By imposing certain conditions on  $q(\underline{r})$  and  $\varphi(\underline{r})$ , (which will be described later), Lebowitz and Penrose showed that in the limit  $\gamma \rightarrow 0$ ,

Thouless (1969), and others on one-dimensional systems with intrinsically long-range potentials which are not of the Kac type.

### C. Metastable States

The rigorous equilibrium theory does not assign any meaning to those portions of the 'van der Waals loop' which Maxwell identified with metastable states. While such metastable states are certainly present in real systems it is difficult to see how to incorporate them in the usual formalism of statistical mechanics. It was shown, however, by Penrose and Lebowitz (1971) that for systems with long range potentials of the type considered here it is possible to treat these states by considering situations in which the system is initially confined to a region  $R$  of the configuration space in which its density is 'roughly' uniform. They proved that in the van der Waals limit,  $\gamma \rightarrow 0$ , such a system, with overall density  $\rho$  in the metastable region of the van der Waals loop, will remain in the region  $R$  with probability one. Its pressure, and other thermodynamic properties, will then be given by the van der Waals equation without the Maxwell construction.

it is sometimes simpler to consider expansions in which the terms are general functions of  $\gamma$  which vanish successively "faster" as  $\gamma \rightarrow 0$ . These expansions can also be formulated in a way which does not require the explicit use of the parameter  $\gamma$  and can thus be used for a general  $w(r)$  in (1.1). While it is not known whether any of these expansions converge for any values of  $\rho$  and  $T$  it is known that they fail in the vicinity of the van der Waals critical point (the terms generally becoming infinite.)

An alternative approach has been to use some kind of closed self consistent approximations which are particularly "reasonable" when the potential  $w(r)$  is long range. These methods usually involve the solution of some sort of integral equation and do not make use of any range parameter  $\gamma$ . Indeed some of these methods precede the introduction of the Kac potential. We shall discuss some of the many approximation methods suitable (or so believed) for systems with long-range potentials in Section IV.

Fig. 8. The composite graph (a) is contained in the graph (b) with hypervertices, which in turn is contained in the graph (c) with chain bonds. (Graph notation is explained in the text).

Fig. 9. The isochore  $v=2v_B$  for the van der Waals equation, the generalized van der Waals equation (5.1) and for Argon (Michels et al.1949; Levelt 1958). Temperatures have been reduced with the Boyle temperature  $T_B$ , volumes with the Boyle volume  $v=[dB_2(T)/dBnT]_{T=T_B}$  (From Hauge and Hemmer, 1966).

Fig.10. Phase transitions predicted by the generalized van der Waals equation (5.1).

Fig.11. (a) The potential (5.8) with a weak Kac potential attached. (b) The range of potential parameters for which two transitions exist (t.p. means triple point).

Fig.12. The reduced critical temperature, density and pressure for simple fluids. The classical values have been determined by requiring the experimental curve to fit the data for Xenon.