Rigorous Treatment of Equilibrium and Metastable States in the

Van der Waals--Maxwell Theory of First Order Phase Transition[*][+]

by

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I. Introduction.

It is the purpose of this talk is to present some work[1,2] which provides a rigorous description of the equilibrium and metastable states of "van der Waals" systems', i.e. systems with long range weak potentials[3]. We consider a classical (or quantum[4]) system of N particles confined to a cubical box of volume Ω, $N \equiv \rho\Omega$, and interacting via a pair potential $v(\underline{r})$ of the form,

$$v(\underline{r}) = q(\underline{r}) + \gamma^{\nu}\varphi(\gamma\underline{r}), \tag{1}$$

where ν is the dimensionality of the space considered and γ^{-1} is a parameter which measures the range of the 'Kac potential' $\varphi(\underline{y})$.

The functions $q(\underline{r})$ and $\varphi(\underline{y})$ are assumed to satisfy the following conditions

$$q(\underline{r}) = \infty, \text{for } r < r_0, \quad |q(\underline{r})| < D_2 \, r^{-\nu-\epsilon}, \text{ for } r > r_0 \tag{2}$$

(the first of these is technical and can probably be weakened, the second is essential)

$$|\varphi(\underline{y})| < D_3 y^{-\nu-\epsilon} \text{ for all } y \tag{3a}$$

$$\varphi(\underline{y}) \text{ is continuous at } y = 0 \tag{3b}$$

$$\alpha \equiv \int\varphi(\underline{y})d\underline{y} \text{ exists as a Riemann integral.} \tag{3c}$$

where r_0, D_2, D_3 and ϵ are positive constants and α may be either positive or negative. To make the final results completely definite it is also necessary to assume that φ satisfies either[5] (4a) or (4b),

$$\widetilde{\varphi}(\underline{k}) = \int\varphi(\underline{y}) \, e^{i\underline{k}\cdot\underline{y}} \, d\underline{y} \geq 0 \tag{4a}$$

$$\widetilde{\varphi}(0) = \underset{\underline{k}}{\text{Minimum }} \widetilde{\varphi}(\underline{k}). \tag{4b}$$

The physically interesting case of an attractive long range potential, $\varphi(\underline{y}) \leq 0$, is a special case of (4b).

We then show that in the van der Waals limit $\gamma \to 0$, taken after

the thermodynamic limit $\Omega \to \infty$, the Helmholtz free energy per unit volume has the form

$$a(\rho,0+) \equiv \lim_{\gamma \to 0} a(\rho,\gamma) \equiv \lim_{\gamma \to 0} \lim_{\Omega \to \infty} \left[\frac{A(\rho\Omega,\Omega,\gamma)}{\Omega}\right]$$
$$= CE\{a^{0}(\rho) + \tfrac{1}{2}\alpha\rho^{2}\} \qquad (5)$$

Here $A(N,\Omega,\gamma)$ is the Helmholtz free energy of the system with N particles at some temperature T (not indicated explicitly): $a^{0}(\rho)$ is the Helmholtz free energy per unit volume in the reference system, i.e. the system with inter-particle potential $q(\underline{r})$, and $CE\{f(\rho)\}$ means, for any function $f(\rho)$, the <u>convex envelope</u> of that function, defined as the maximal convex function not exceeding f:

$$CE\{f(\rho)\} \equiv \underset{\phi(\cdot)}{\text{Max}} \; \phi \; \text{ for each value of } \rho$$

$$\left\{ \begin{array}{l} \phi(\cdot) \text{ is convex} \\ \phi(\xi) \leq f(\xi) \text{ for all } \xi \end{array} \right\} \qquad (6)$$

Since the maximum of any family of convex functions is itself convex, the function $CE\{f(\rho)\}$ is convex. If $f(\rho)$ is convex, then $CE\{f(\rho)\}$ and $f(\rho)$ coincide; otherwise the graph of $CE\{f(\rho)\}$ consists partly of convex segments of the graph of $f(\rho)$ and partly of segments of double tangents of this graph (Fig. 1). The construction of $CE\{f(\rho)\}$ from $f(\rho)$ is sometimes called the <u>double tangent construction</u>, or Gibbs construction.

The corresponding pressure $p(\rho,0+) = \lim_{\gamma \to 0} p(\rho,\gamma)$ is given by $p(\rho,0+) = \rho^{2} \frac{\partial}{\partial \rho} [a(\rho,0+)/\rho]$ which corresponds to applying the Maxwell equal area construction to the generalized van der Waals pressure $\widetilde{p}(\rho) = p^{0}(\rho) + \tfrac{1}{2}\alpha\rho^{2}$, (Fig. 2).
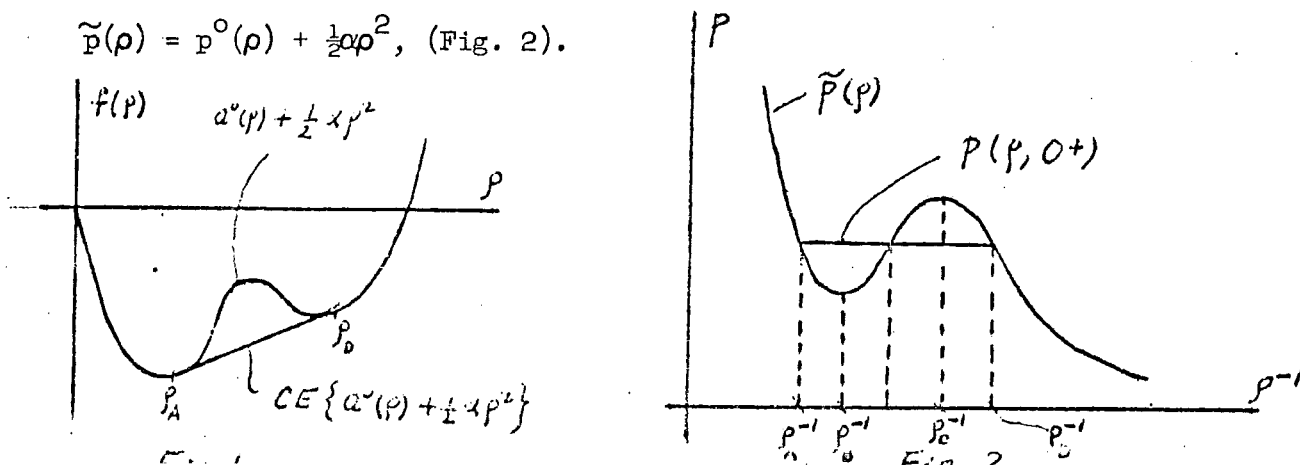
II. Methods of Proof.

Our method of proof consists in finding upper and lower bounds for $a(\rho,\gamma)$ which, under the conditions on the potential assumed before, coincide in the limit $\gamma \to 0$. To accomplish this we divide the cubical volume Ω into M smaller cubical regions (cells) $\omega_1,\ldots,\omega_M$ each of volume ω
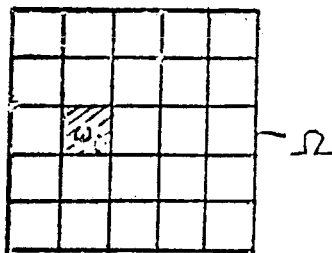
Fig. 3

(Fig. 3). We then prove our results by taking a sequence of limits $\Omega \to \infty$, $\gamma^{-1} \to \infty$, $\omega \to \infty$ in the order indicated, i.e. the lengths appearing in the problem satisfy the inequalities

$$r_o \ll \omega^{1/\nu} \ll \gamma^{-1} \ll \Omega^{1/\nu}. \tag{7}$$

The range of the Kac potential is thus very small compared to the size of the container but very large compared to the size of the cells, ω, which are in turn very large compared to the 'range' of $q(\underline{r})$.

The size of the cells ω is not an intrinsic parameter of the problem and is only introduced as an aid in the calculations where it plays the central role of separating the total interaction energy of the system

$$V = \sum_{i<j} [q(\underline{r}_{ij}) + \gamma^{\nu}\varphi(\gamma\underline{r}_{ij})] \tag{8}$$

into a part coming from interactions between particles in the same cell and part coming from interactions between cells. This leads, after taking the triple limit of $\Omega^{1/\nu} \gg \gamma^{-1} \gg \omega^{1/\nu} \to \infty$, to a 'corresponding' division in the Helmholtz free energy given in (5): $a^o(\rho)$ being a purely intra-cell affair while $\frac{1}{2}\alpha\rho^2$ is the interaction energy per unit volume between cells when the system is uniform on the scale γ^{-1}. For values of ρ (and T) for which

$$a(\rho,0+) = CE\{a^O(\rho) + \tfrac{1}{2}\alpha\rho^2\} \neq a^O(\rho) + \tfrac{1}{2}\alpha\rho^2, \qquad (9)$$

the value $a(\rho,0+)$ coincides with that obtained by assuming the system to consist of two phases with densities ρ_A and ρ_D (Figs. 1 and 2). That this is indeed the state of the system can be seen by considering the form of the distribution functions at these densities[1] and more explicitly from the discussion which follows.

III. Restricted Configurations.

Starting from the partition functions of a system with an inter-particle potential given in (1) we have obtained a convex $a(\rho,0+)$ which contains, for suitable $a^{o}(\rho)$ and α, a linear part leading to pressure isotherms containing a horizontal segment, (cf. Figs. (1) and (2) for $\rho_A < \rho < \rho_D$). No meaning at all is attached to that part of the curve $a^{o}(\rho) + \frac{1}{2}\alpha\rho^2$ which lies above the curve $CE\{a^{o}(\rho) + \frac{1}{2}\alpha\rho^2\}$ or to the corresponding part of the pressure curve $p^{o}(\rho) + \frac{1}{2}\alpha\rho^2$. Traditionally however the parts of these curves (actually of similar curves obtained from the original van der Waals-Maxwell theory) lying between $\rho_A < \rho < \rho_B$ and $\rho_C < \rho < \rho_D$ are assumed to represent the properties of metastable states of uniform density corresponding to the supercooled vapour and the superheated liquid respectively, the densitites ρ_B and ρ_C being the limits of metastability[6,7]. We shall now show how it is possible to give a rigorous meaning to these states by considering the properties of our system when it is confined to a restricted region of the configuration space.

To do this we imagine that our system of N particles in the box of volume Ω is _restricted_ to a region in configuration space specified by constraints on the number, N_i, of particles in the cells $\omega_i, i=1,\ldots,M$, (Fig. 3). A general restriction of this kind is expressed by the requirement that there be a fraction p_j of the cells, $j=1,\ldots,m$ whose densities $\rho_i \equiv N_i/\omega$ lie in the interval $\Delta_j = (\rho_{(j)}, \rho^{(j)})$, i.e.

$$\rho_{(j)} \leq \rho_i \equiv N_i/\omega \leq \rho^{(j)} \qquad \text{for } p_j M \text{ cells.} \qquad (10)$$

with $\sum\limits_{j=1}^{M} p_j = 1$ and $p_j M$ an integer. Since there are altogether N particles

in the system we must choose the intervals Δ_j in such a way that there exist densities ξ_j in Δ_j

$$\rho_{(j)} \leq \xi_j \leq \rho^{(j)} \tag{11}$$

for which

$$\sum_{j=1}^{m} p_j \, \xi_j = \rho. \tag{12}$$

We can now define a restricted partition function $Z'(\rho\Omega, \Omega, \gamma | \{p_j, \Delta_j\})$ for which the integrations in configuration space are limited to the regions satisfying the condition (10). Z' is thus, unlike Z, a function of the cell size ω. It is now possible to find bounds on the free energy per unit volume for the restricted partition function in the triple limit discussed before. We find then,

$$a(\rho, 0+) \leq a'(\rho, 0+ | \{p_j, \Delta_j\}) = \lim_{\omega \to \infty} \lim_{\gamma \to 0} \lim_{\Omega \to \infty} [\frac{\ln Z'(\rho\Omega, \Omega, \gamma | \{p_j, \Delta_j\})}{\Omega}]$$

$$\leq \underset{\{\xi_j\}}{\text{Min}} \{\sum_{j=1}^{m} p_j [a^o(\xi_j) + \tfrac{1}{2}\alpha\xi_j^2 + g_j(\xi_j)] \tag{13}$$

where

$$g_j(\xi) = \begin{cases} 0 \text{ for } \xi \text{ in } \Delta_j \\ \infty \text{ for } \xi \text{ not in } \Delta_j \end{cases} \tag{14}$$

and the minimum is taken over all possible values of the ξ_j satisfying (12). Similarly it is shown that

$$a'(\rho, 0+ | \{p_j, \Delta_j\}) \geq \underset{\{\xi_j\}}{\text{Min}} \{\sum_{j=1}^{m} p_j \text{CE}\{a^o(\xi_j) + \tfrac{1}{2}\alpha\xi_j^2 + g_j(\xi_j)\}\} \tag{15}$$

If we now let the intervals Δ_j shrink to the points ξ_j satisfying (12) the upper bounds (13) and (14) coincide yielding

$$a'(\rho, 0+ | \{p_j, \xi_j\}) = \sum_{j=1}^{m} p_j [a^o(\xi_j) + \tfrac{1}{2}\alpha\xi_j^2] \tag{16}$$

IV. Stable Metastable and Unstable Macroscopic States

We shall define the macroscopic states, or simply states, of our system $S(p_i, \xi_i, \rho)$ by the distribution $\{p_i, \xi_i\}, i=1,\ldots,m$, satisfying (12). This gives (in the triple limit discussed before) the fraction of cells, or systems volume, p_i at density ξ_i. To each state there will then correspond a free energy per unit volume $a'(\rho,0+|\{p_i,\xi_i\})$ given in (16).

For any given constraint $C\{p_j', \Delta_j, \rho\}, j=1,\ldots,n$, that there be a fraction of cells p_j' in the density interval Δ_j there will be in general many states $S\{p_i, \xi_i, \rho\}, i=1,\ldots,m$, which will satisfy this constraint, with m not necessarily equal to n, it is only necessary that $\sum_{\Delta_j} p_i = p_j$ the summation being taken over all those i for which ξ_i is in Δ_j. We shall indicate that a state $S\{p_i, \xi_i, \rho\}$ satisfies a certain constraint $C\{p_j', \Delta_j, \rho\}$ by writing

$$S\{p_i, \xi_i, \rho\} \in C\{p_j', \Delta_j, \rho\} \qquad (17)$$

Thus all states satisfy the constraint $p_1' = 1$, $\Delta_1 = (0, \infty)$.

A state will be called stable $S_s\{p_i, \xi_i, \rho\}$ if its corresponding $a'(\rho,0+|\{p_i,\xi_i\})$ is lower than that for any other state. A state will be called metastable $S_m\{p_i, \xi_i, \rho\}$ if its corresponding $a'(\rho,0+|\{p_i,\xi_i\})$ is lower than that for any other state $S\{p_j, \xi_j, \rho\}$ <u>satisfying</u> the constraint $C_m\{p_i, \Delta_i, \rho\}$ where the p_i are the same numbers as the p_i of the metastable state and the Δ_i are intervals centered on the ξ_i of the metastable state of width greater than some positive number 2Δ, i.e. it is possible to get from the state $S_m\{p_i, \xi_i, \rho\}$ to a 'neighboring state' $S(p_j, \xi_j, \rho) \in C_m\{p_i, \Delta_i, \rho\}$ without changing the density in any cell by more than Δ. A maximally unstable state $S_u\{p_i, \xi_i, \rho\}$ is one whose corresponding $a'(\rho,0+|\{p_i,\xi_i,\})$ is greater than that of all other states in its 'neighborhood'. We shall call all the three types of

states described here extremal states.

Consider now the case where the functions $a^O(\rho) + \frac{1}{2}\alpha\rho^2$ have the form shown in Fig. 1, (e.g. there is only one interval in which the graph is a straight line; the results for more general situations are immediate). It is then possible to show that: 1) For densities ρ such that $0 < \rho < \rho_A$ or $\rho_D < \rho$, region I, where $a^O(\rho) + \frac{1}{2}\alpha\rho^2$ coincides with $CE\{a^O(\rho) + \frac{1}{2}\alpha\rho^2\}$, the stable state is one of uniform density $p_1=1, \xi_1=\rho$; 2) For densities ρ such that $\rho_A < \rho < \rho_B$ or $\rho_C < \rho < \rho_D$, region II, where $CE\{a_o(\rho) + \frac{1}{2}\alpha\rho^2\}$ is linear and there is always some $\Delta > 0$ such that $a^O(\rho) + \frac{1}{2}\alpha\rho^2$ is convex in an interval of size 2Δ centered on ρ the stable state is that of a two phase system at densities ξ_1 and ξ_2, $\xi_1 = \rho_A$, $\xi_2 = \rho_D$, $p_1 = (\rho_B-\rho)/(\rho_B-\rho)$ $p_2 = 1-p_1$, and there is a metastable state corresponding to the system being a uniform density ρ; 3) For densities in the range $\rho_B < \rho < \rho_C$, region III, $CE\{a^O(\rho) + \frac{1}{2}\alpha\rho^2\}$ is linear and $a^O(\rho) + \frac{1}{2}\alpha\rho^2$ is concave in an interval of size 2Δ about ρ, the stable state is of the same form as in region II and the uniform state is maximally unstable.

In order to justify the naming of stable and metastable states we note that the probability $W(C)$ of the unconstrained system being in a region of configuration space $\mathcal{R}$, corresponding to a given constraint $C\{p_i,\Delta_i,\rho\}$, is given by

$$\ell n W(C) = -\beta\Omega \left[\Omega^{-1}A\cdot(\rho\Omega,\Omega,\gamma|\{p_i,\Delta_i\})-\Omega^{-1}A(\rho\Omega,\Omega,\gamma|\{p_i,\Delta_i\})\right] \qquad (18)$$

It follows then from (16), the definition of a limit and the uniqueness of the stable state, for sufficiently large ω, γ^{-1} and Ω satisfying (7) that if the stable state $S_s\{p_i,\xi_i,\rho\} \notin C\{p_j,\Delta_j,\rho\}$ then the term in the square bracket on the right side of (18) will be larger than some positive number $h > 0$. Hence

$$\ln W(C) \leq -\beta \Omega h \text{ if } S_s\{p_i,\xi_i,\rho\} \notin C\{p_j,\Delta_j,\rho\} \tag{19}$$

and the probability of the system being in that region of configuration space will be arbitrarily small for sufficiently large Ω. Conversely the probability that the system is in the part of configuration space complimentary to R will be arbitrarily close to unity. We may thus conclude that the stable state will have unit probability in the triple limit considered here. A similar analysis may be carried out for the probability of the metastable when the system is constrained to be in the 'neighborhood' of the uniform state.

These considerations can be used to understand (and perhaps prove rigorously) the form of the distribution functions given in ref. 1. They also indicate that in the metastable state the distribution functions will remain the same as in the reference system. No indication is given, however, about the dynamics, i.e. relaxation rate, of metastable states. We believe, however, that if the system is initially in the vicinity of the uniform (metastable) state then the rate per unit volume at which the system will leave this state (by droplet or bubble formation) will vanish in the triple limit considered here[2].

V. Finite Range Kac Potential.

In conclusion I would like to mention that Lebowitz, Stell and Baer have developed[7] a formal graphical method for obtaining expansions in γ of the correlation functions and thermodynamic properties of a system with interparticle potential (1). These expansions have meaning only for those values of ρ and T for which the van der Waals system, $\gamma \to 0$, is uniform. The convergence of the expansion has not been investigated.

References

1. J.L. Lebowitz and O. Penrose, "Rigorous Treatment of van der Waals'-Maxwell Theory of First Order Phase Transition" to appear in J. Math. Phys.

2. O. Penrose and J.L. Lebowitz, "Rigorous Treatment of Metastable States for van der Waals Systems", in preparation.

3. As will be recognized immediately by the cognoscenti our analysis is greatly indebted to the work of Kac, Uhlenbeck and Hemmer J. Math. Phys. 4, 216 (1963) and of van Kampen, Phys. Rev. 135, 362 (1964).

4. While this talk is couched in the language of classical fluids our results apply also to lattice gases (and thus to Ising spin systems) and to quantum systems. The proof for quantum systems, which requires some new intermediate steps, was given by E. Lieb, "Quantum Mechanical Extension of the Lebowitz-Penrose Theorem on the Van der Waals Theory" to be published. In Lieb's proof it is necessary to assume that $a^o(\rho)$ is independent of whether the wave function or its normal derivative are assumed to vanish on the boundary of Ω. While this seems 'obvious' it has not yet been proven.

5. When (4) is not satisfied our lower bound on $a(\rho, 0+)$ may not coincide with the upper bound for some values of the density and temperature.

6. J.C. Maxwell, Scientific Papers, (Dover Reprint, New York) p. 425, see also M. Fisher, "The Theory of Condensation" Lecture given at the University of Kentucky (Spring, 1965) and J. Langer's article in this volume.

7. J.L. Lebowitz, G. Stell and S. Baer, J. Math. Phys. 6, 1282 (1965); G. Stell, J.L. Lebowitz, S. Baer and W. Theuman, "Seperation of the Interaction Potential into Two Parts in Statistical Mechanics, II, to be published.