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A Gibbsian formulation of thermostatics

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Abstract. We present a semi axiomatic formulation of thermostatics, starting from a sufficiently general point of view to be able to express how the laws of thermostatics impose a certain structure on the statemanifold. We then exemplify, by doing the explicite construction for the van der Waal fluid, how the thermostatic description of a system appears as a parametrization of the equilibrium states of the corresponding thermodynamical system.

1. Introduction

To describe a given physical system, means to give a model that reflects its constitution and simulates its behaviour. The model itself is formulated in terms of “concepts” defined in a (physical) theory that is designed to describe the possible behaviours of a class of physical systems.

The framework of a well-formulated theory consists of a mathematical structure and an interpretation of its mathematical symbols. It can be decomposed into a setting which expresses the basic structure, and a set of ‘physically’ motivated postulates which summarizes the restrictions to the possible behaviours of the systems the theory is designed to describe.

The division between setting and postulates in a given framework is not apriori given, but depends on conventions, taste, style and convenience. The choice we have made in the present formulation of thermostatics, has in particular, been motivated by a wish to extract as much information as possible from the ‘laws of thermostatics’.

The setting is defined by the following elements. A six-dimensional differentiable manifold E is given in terms of a set of coordinates, which are identified as the entropy S , mass M , volume V , temperature T , chemical potential μ and pressure p . As observables for a thermostatic system these are known to be independent; in fact, it is assumed that there are apriori three (functional) relations between them, i.e. the states form a three-dimensional submanifold L of E . The notion of a process is defined. It is assumed to be represented by a piecewise analytic curve $c: [t_1, t_2] \rightarrow E$ and lying on L . We then

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introduce the energy as a quantity which is represented as a functional on the processes, i.e. $\Delta E(c)$ denotes the variation of energy along the process c . Since we are working with at least piecewise differentiable submanifolds and curves, it is natural to assume that $\Delta E(c)$ is represented by an integral over c of a one-form Θ_U . We are completing the setting by assuming that $\Theta_U = T dS + \mu dM - p dV$. This specification of Θ_U belongs to an operational definition of the thermostatic observables.

The next step is to investigate the structure imposed on this setting by the thermostatic postulates. We consider the 'first law of thermostatics' which says that the variation of energy along any 'closed' process is zero. Let $\pi_F: E \rightarrow N_F = \{(M, V, T)\}$ be the canonical foliation, we then also assume as part of this postulate that there exist at least one state 'over' each $(M, V, T)^2$.

A crucial point now is what is meant by a closed process. In fact by this we do not mean that the curve representing the process is closed in E (or on L), but only that the 'projection' of the curve onto the submanifold $N_F = \{(M, V, T)\}$ is closed. The analysis of the consequences of the energy postulate shows that the restriction of Θ_U to the state manifold L must be exact since $\Delta E(c) = 0$ for all curves that are closed on L (these belong all to the class of closed processes). This means that L is a lagrangian submanifold of the symplectic manifold $(E, d\Theta_U)^3$. Secondly, if we had a situation where L 'folds' over N_F , i.e. that we for a subset of N_F have more than one state over each (M, V, T) , then we could easily exhibit curves that describe a closed process but for which $\Delta E(c) \neq 0$. Since such situations is excluded by the energy postulate, we are forced to conclude that L can not 'fold' over N_F , i.e. there can exist only one state over each (M, V, T) . Accordingly, there exists a bijection $\varphi_F: N_F = \{(M, V, T)\} \rightarrow L$.

The exactness of the restriction of Θ_U to L is equivalent to the Maxwell relations $d\Theta_U|_L = 0$, and implies that there exists generating functions (thermostatic potentials) for L . This is for the choice of variables (M, V, T) , the Helmholtz free energy function $F: N_F \rightarrow \mathbb{R}$ which because of the existence of the bijection φ_F is globally defined. It thus follows that a model of a thermostatic system is given by the specification of a free energy function.

The second postulate (to be referred to as the second law of thermostatics), is from the point of view of thermodynamics a stability condition. It appears as a corollary to the second law of thermodynamics, and is expressed as $\partial_T^2 F < 0$ [3]. A consequence of this statement, which can be considered as an equivalent statement of the second law of thermostatics, is that the canonical projection of L onto the 'submanifold' $N_U = \{(S, M, V)\}$ is nonsingular, i.e. there exists a canonical bijection $N_F \rightarrow N_U = \{(S, M, V)\}$. An immediate result of this is the existence of a second global generating function, the energy function U .

²⁾ The reason why we chose the variables M, V, T is that these are most directly accessible to observation.

³⁾ Definition [1, 2]: Let N^n and M^{2n} be differentiable manifolds ω a symplectic form on M and let $\varphi: N \rightarrow M$ be an embedding. The submanifold $\varphi(N) \subset M$ is said to be a lagrangian submanifold of (M, ω) and φ a lagrangian embedding if $\varphi^* \omega = 0$.

The main difference between the formulation of thermostatics and more traditional formulations, seems to be that we consider as an object the total space E , endowed with a symplectic structure $\omega = d\Theta_U$, defined by the energy one-form, and that the states form a lagrangian submanifold of the symplectic manifold (E, ω) . This formulation is justified by the fact that the formalism of lagrangian manifolds gives the setting for a global theory of generating functions and Legendre transformations which is at the core of any mathematical formulation of thermostatics. Starting with a more general setting also makes it possible to extract more information from the energy postulate, i.e. we can also infer that $\{(M, V, T)\}$ gives a complete and unique parametrization of the states. It seems to us to be quite important to be able to make such a statement, which is generally true only for N_F and N_U (as a consequence of the second postulate). In fact, the other canonical projections of L (onto $\{(V, T, \mu)\}$ and $\{(T, \mu, p)\}$) might be singular. If this is the case, the system is said to possess 'phase-transitions of the first kind'.

The thermostatic statemanifold is from the point of view of a thermodynamical description of a system, a parametrization of the equilibrium states, and its structure is inherited from a similar structure on the thermodynamical statemanifold. The part of this paper that we have described so far is however, an exposition of the structure of thermostatics in its own right. The first one that seems to have undertaken such a study is J. W. Gibbs [4]. Although the mathematical formulation that we have given is different from that of Gibbs, it seems to us that both the aim and the spirit of the formulation is the same.

In addition to giving a formulation of thermostatics however, we also illustrate the relation to thermodynamics by the explicite construction of the thermostatic statemanifold of the van der Waal fluid as a parametrization of its equilibrium states. To make this construction we must appeal to the thermodynamical description of the fluid.

Part I. The Framework of thermostatics

2. The setting

Definition. A thermostatic system is by assumption associated with

- (i) a statemanifold L which is represented as a (piecewise analytic) C^0 -submanifold of the manifold⁴⁾

$$E = \{(S, M, V, T, \mu, p) \in \mathbb{R} \times \mathbb{R}^3 \times \mathbb{R} \times \mathbb{R}_+\}$$

- (ii) the *extensive* observables entropy S , mass M and volume V , and the corresponding *intensive* observables temperature T , chemical potential μ and pressure p , which are represented by the restriction of the functions

⁴⁾ $\mathbb{R}_+ = \langle 0, \infty \rangle$.

$$E \rightarrow \mathbb{R},$$

$$\hat{S}(S, M, V, T, \mu, p) = S$$

$$\vdots$$

$$\hat{p}(S, M, V, T, \mu, p) = p$$

to L ;

- (iii) a set of processes, i.e. the piecewise analytic curves $c: [t_1, t_2] \mapsto E$ such that $c(t) \in L \forall t \in [t_1, t_2]$;
- (iv) the observable of energy, whose variation ΔE along a process is measured by the 1-form

$$\Theta_U = T dS + \mu dM - p dV$$

i.e.

$$\Delta E(c) = \int_C \Theta_U = \int_{t_2}^{t_1} \Theta_U(\dot{c}) \circ c \, dt$$

Notice that the energy form is a sum of the 1-forms TdS , μdM and $-p dV$ which measure the change of heat, of chemical energy and of work along the processes. We would also like to remark that other settings can be considered. For alternatives see for example [3] and [4].

3. The first law of thermostatics

Definition. Let π_F denote the projection (submersion)

$$E \rightarrow N_F = \{(M, V, T) \in \mathbb{R}_+^3\}$$

a process is said to be closed if

$$\gamma_F = \pi_F \circ c: [t_1, t_2] \mapsto N_F$$

is closed, i.e. $\gamma_F(t_1) = \gamma_F(t_2)$.

Postulate 1S (The First Law of Thermostatics).

- (a) The variation of energy is zero along any closed process c , i.e.

$$\Delta E(c) = 0$$

- (b) $\pi_F|_L: L \rightarrow N_F$ is onto (surjectiv).

An equivalent statement is expressed by the following theorem which we will refer to as the first fundamental theorem of thermostatics.

Theorem. *Postulate 1S is equivalent to the following statements:*

- (i) L is a Lagrangian submanifold of $(E, d\Theta_U)$
- (ii) $\pi_F|_L: L \rightarrow N_F$ is a homeomorphism.

Proof.

- (i) Any closed curve on L i.e. for which $c(t_1) = c(t_2)$ is a closed process. That $\Delta E(c) = 0$ for all closed curves on L implies that $\Theta_U|_L$ must be exact, i.e. L is Lagrangian, $d(\Theta_U|_L) = d\Theta_U|_L = 0$.
- (ii) All closed processes must be closed curves on L in order to satisfy $\Delta E(c) = 0$. That means that L cannot fold over N_F ■.

Corollary. *There exists a global generating function⁵⁾ $F: N_F \rightarrow \mathbb{R}$, the (Helmholz) free energy, i.e. there exists a lagrangian embedding $\phi_F: N_F \rightarrow E$ such that $\phi_F(N_F) = L$ and $\phi_F^* \Theta_F = dF$ for $\Theta_F = \Theta_U - d(TS)$.*

Proof. The existence of the embedding ϕ_F follows from (ii). Moreover, from (i) follows that ϕ_F is Lagrangian; thus, the existence of F is a consequence of Poincaré's lemma; i.e.

$$\phi_F^* d\Theta_F = d\phi_F^* \Theta_F = 0$$

$$F: N_F \rightarrow \mathbb{R} \text{ such that } \phi_F^* \Theta_F = dF$$

Moreover, by comparing coefficients in $\phi_F^* \Theta_F = dF$ we find that ϕ_F is defined by

$$\phi_F: N_F \rightarrow E; (M, V, T) \mapsto (-\partial_T F(.), M, V, T, \partial_M F(.), -\partial_V F(.)) \quad \blacksquare$$

The above theorem assures the existence of a representation, the free energy representation.

Definition. In the free energy representation

- (i) the statemanifold L is characterized by

$$L = \{(S, M, V, T, \mu, p) \in E \mid S + \partial_T F = 0, \mu - \partial_M F = 0, p + \partial_V F = 0\}$$

- (ii) the observables are represented by the functions $N_F \rightarrow \mathbb{R}$ defined by

$$S_F(M, V, T) = -\partial_T F(M, V, T)$$

$$M_F(M, V, T) = M$$

$$V_F(M, V, T) = V$$

$$T_F(M, V, T) = T$$

$$\mu_F(M, V, T) = \partial_M F(M, V, T)$$

$$p_F(M, V, T) = -\partial_V F(M, V, T).$$

⁵⁾ Actually it is a priori defined up to an integration constant.

4. The second law

The Second Law of Thermodynamics expresses a dynamical condition: that the entropy is a monotonically increasing function of time during the evolution of an isolated system. The consequence of this for the structure of thermostatics is expressed by the following postulate.

Postulate 2S. The Second Law of Thermostatics: The stability condition

$$\partial_T^2 F < 0$$

is satisfied.

Theorem. The projection π_U of L into $N_U = \{(S, M, V) \in \mathbb{R} \times \mathbb{R}_+^2\}$ is onto and nonsingular, i.e.

$$\pi_U | L : L \rightarrow N_U$$

is a homeomorphism.

Proof. The above statement follows from the fact that

$$\phi_{FU} : N_F \rightarrow N_U; (M, V, T) \mapsto (-\partial_T F(M, V, T), V, T)$$

is a homeomorphism; in fact, the Jacobian determinant $j(\phi_{FU})$ of ϕ_{FU} is $-\partial_T^2 F$ which according to the second law is positive. ■

Corollary. There exists a global generating function⁶⁾ $U : N_U \rightarrow \mathbb{R}$, the (internal) energy, i.e.

$$\exists \phi_U : N_U \rightarrow E$$

such that

$$\phi_U(N_U) = L \quad \text{and} \quad \phi_U^* \Theta_U = dU$$

Proof. The proof of this statement is essentially the same as the corresponding corollary of the last paragraph. ■

The next theorem expresses that the generating functions F and U are related by a Legendre transformation.

Theorem. Let $\phi_{UF} : N_U \rightarrow N_F$ denote the inverse of ϕ_{FU} ; then,

$$U = F \circ \phi_{UF} - S_U T_F \circ \phi_{UF}$$

where $S_U : N_U \rightarrow \mathbb{R}$, is defined by $S_U(S, M, V) = S$.

⁶⁾ U is defined up to an integration constant.

Proof. It is a consequence of the fact that U and F are generating functions associated with the 1-forms Θ_U and Θ_F which satisfy $\Theta_U = \Theta_F + d(ST)$. ■

Theorem. *The map*

$$\tilde{\phi}: E \rightarrow E; (S, M, V, T, \mu, p) \mapsto (U(S, M, V), M, V, T, \mu, p)$$

is a diffeomorphism of class C^1 ; moreover, the projection of L into $N_S = \{(U, M, V) \in \mathbb{R} \times \mathbb{R}_+^2\}$ is nonsingular.

Proof. Follows from the fact that

$$j(\tilde{\phi}) = \partial_S U = T > 0 \quad \blacksquare$$

Corollary. *There exists a global generating function $\hat{S}: N_S \rightarrow \mathbb{R}$, the entropy, i.e.*

$$\phi_S: N_S \rightarrow E$$

such that

$$\phi_S(N_S) = L \quad \text{and} \quad \phi_S^* \Theta_S = dS$$

where

$$\Theta_S = \frac{1}{T} dU - \frac{\mu}{T} dM + \frac{p}{T} dV.$$

Remark. The global existence theorems for the energy and entropy generating functions assures the existence of an energy and an entropy representation defined in analogy with the free energy representation.

5. The homogeneity postulate

In thermodynamics the energy and the extensive variables are defined in terms of densities. A consequence of this for thermostatics is expressed by the following postulate.

Postulate 3S. The energy function is a first order homogeneous function,

$$U(\lambda S, \lambda M, \lambda V) = \lambda U(S, M, V) \quad \forall \lambda \in \mathbb{R}_+$$

An immediate consequence of this postulate is that it fixes the integration constants referred to in the preceding paragraphs. However, it has further important consequences.

Theorem. *The generating functions F and S satisfy the homogeneity conditions*

$$\begin{aligned} F(\lambda M, \lambda V, T) &= \lambda F(M, T, V) \\ S(\lambda U, \lambda M, \lambda V) &= \lambda S(U, M, V) \end{aligned} \quad \forall \lambda \in \mathbb{R}_+$$

Proof. Follows from their relation to U . ■

Theorem. *There exists 'density' functions u , f and s such that*

$$U(S, M, V) = Vu\left(\frac{S}{V}, \frac{M}{V}\right),$$

$$F(M, V, T) = Vf\left(\frac{N}{V}, T\right),$$

$$S(U, M, V) = Vs\left(\frac{U}{V}, \frac{M}{V}\right).$$

Proof. Choose $\lambda = 1/V$; then,

$$\frac{1}{V} U(S, M, V) = U\left(\frac{S}{V}, \frac{M}{V}, 1\right)$$

or

$$U(S, M, V) = U\left(\frac{S}{V}, \frac{M}{V}, 1\right)$$

i.e.

$$u\left(\frac{S}{V}, \frac{M}{V}\right) = U\left(\frac{S}{V}, \frac{M}{V}, 1\right)$$

The same for the F and S . ■

Using this we can in some sense reduce the state space by one dimension.

Theorem. *Consider the map*

$$\phi: E \rightarrow E; (S, M, V, T, \mu, p) \rightarrow (s, \rho, V, T, \mu, u) \quad (12)$$

defined by

$$s = \frac{S}{V}$$

$$\rho = \frac{M}{V}$$

$$u = -p + T \frac{S}{V} + \mu \frac{M}{V}$$

and let

$$\tilde{\theta}_u = (Tds + \mu d\rho)V + u dV$$

then,

$$\phi^* \tilde{\theta}_u = \Theta_U.$$

Proof. By inspection. ■

This shows that all the information contained in the generating function U is also contained in the function

$$u: \mathbb{R} \times \mathbb{R}_+ \rightarrow \mathbb{R}; (s, \rho) \mapsto u(s, \rho)$$

which is a generating function with respect to the 1-form $T ds + \mu d\rho$. Thus, given u , the intensive variables are represented by the functions $\mathbb{R} \times \mathbb{R}_+ \rightarrow \mathbb{R}$ defined by

$$T(s, \rho) = \partial_s u(s, \rho)$$

$$\mu(s, \rho) = \partial_\rho u(s, \rho)$$

$$p(s, \rho) = -u(s, \rho) + s\partial_s u(s, \rho) + \rho\partial_\rho u(s, \rho)$$

Moreover, f and s can be represented as generating functions with respect to the 1-forms $-sdT + \mu d\rho$ and $\frac{1}{T}du - \frac{\mu}{T}d\rho$.

6. The van der Waal fluid

A model of a classical thermodynamic fluid without internal degrees of freedom is defined by giving for example the free energy density

$$f: \mathbb{R}_+^2 \rightarrow \mathbb{R}$$

The equilibrium states of the system is according to the second law of thermodynamics the maxima of the entropy with respect to a class of variations that leaves invariant the total energy, the total momentum, the total angular momentum and the total mass, and which also contain the local deformations. They are a priori most easily established in the entropy representation, however, takes a more simple form in the free energy representation where they are expressed by [5].

(i) the extremal conditions

$$\nabla_i T(x^i) = 0$$

$$\nabla_i \partial_\rho f(\rho(x^i), T(x^i)) = 0$$

$$\nabla_i (-f(\rho(x^i), T(x^i)) + \rho(x^i) \partial_\rho f(\rho(x^i), T(x^i))) = 0$$

(ii) the stability condition

$$\partial_\rho^2 f(\rho(x^i), T(x^i)) > 0.$$

The first extremal condition implies that $T(x^i) = T = \text{const.}$; thus, if we denote by f the family of functions defined by $f_T(\rho(x^i)) = f(\rho(x^i), T)$, then the remaining extremal conditions read

$$\partial_\rho f_T(\rho(x)) = \mu \text{ \& \; } -f_T(\rho(x)) + \rho(x) \partial_\rho f_T(\rho(x)) = p \quad (1)$$

Clearly, a solution to (1) is $\rho(x) = \rho$; however, a priori $\rho(x)$ could also be “piecewise” homogeneous, i.e.

$$\rho(x) = \rho_1 \chi_{\Delta_1}(x) + \rho_2 \chi_{\Delta_2}(x) + \dots$$

is the characteristic function where χ_{Δ_i} , $\bigcup_i \Delta_i = \mathcal{D}$ and $\Delta_i \cap \Delta_j = \emptyset$ when $i \neq j$. In that case, the solution must satisfy the “jump” conditions

$$\begin{aligned} \mu &= \partial_\rho f_T(\rho_1) = \partial_\rho f_T(\rho_2) = \dots \\ p &= -f_T(\rho_1) + \rho_1 \partial_\rho f_T(\rho_1) = -f_T(\rho_2) + \rho_2 \partial_\rho f_T(\rho_2) = \dots \end{aligned} \quad (2)$$

over the mass-density discontinuities.

To discuss these jump conditions, we need to consider the families of maps $\mathbb{R}_+ \rightarrow \mathbb{R}(\mathbb{R}_+)$ defined by

$$\begin{aligned} \psi_T(\rho) &= \partial_\rho f_T(\rho) \\ \phi_T(\rho) &= -f_T(\rho) + \rho \partial_\rho f_T(\rho) \end{aligned}$$

We first observe that

$$\psi'_T(\rho) = \partial_\rho^2 f_T(\rho) \text{ \& } \phi'_T(\rho) = \rho \partial_\rho^2 f_T(\rho)$$

thus, ψ_T and ϕ_T are 1 – 1 maps on the same domains, and it is sufficient to study only one of them.

Definition. Let $T = g(\rho)$ denote the solution of $(\partial_\rho^2 f)(\rho, T) = 0$. The points $(\rho_c, T_c = g(\rho_c)) \in \mathbb{R}_+^2$ such that $g'(\rho_c) = 0$ are called critical.

We will continue our discussion with explicit reference to the van der Waals fluid whose free energy density is defined by

$$f(\rho, T) = -c_1 \rho T \left\{ 1 + \ln \left((c_2 T)^{1/\gamma-1} \left(\frac{1}{\rho} - \beta \right) \right) \right\} - \alpha \rho^2$$

where α, β, ϕ, c_1 and c_2 are positive constants. The family of functions ϕ_T is then defined by

$$\phi_T(\rho) = \frac{c_1 T}{\frac{1}{\rho} - \beta} - \alpha \rho^2$$

and one verifies easily that the van der Waals model has only one critical point

$$(\rho_c, T_c) = \left(\frac{1}{3\beta}, \frac{8\alpha}{27c_1\beta} \right)$$

Let $\phi: N'_F \rightarrow \mathbb{R}_+$; $(\rho, T) \rightarrow \phi(\rho, T) = \phi_T(\rho)$. The graph of ϕ is the surface

$$\{(\rho, T, p) \in N'_F \times \mathbb{R}_+ \mid p - \phi(\rho, T) = 0\}$$

in $N'_F \times \mathbb{R}_+$, a constant T -slice of which is defined by the graph of the function ϕ_T . For $T > T_c$, ϕ_T is monotonically increasing; for $T < T_c$ however, the graph of

ϕ_T has the form⁷⁾

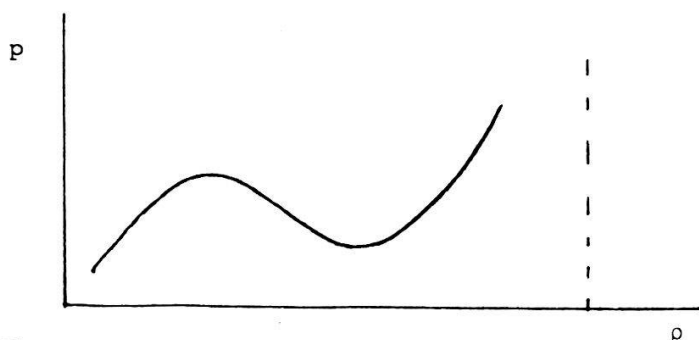


Figure 1

and $\phi'_T = 0$ is seen to have two solutions for each T corresponding to the relative minimum and maximum of the graph. Tracing the projection of the maxima and the minima onto the ρ -axis against T , we get the spinodal curve

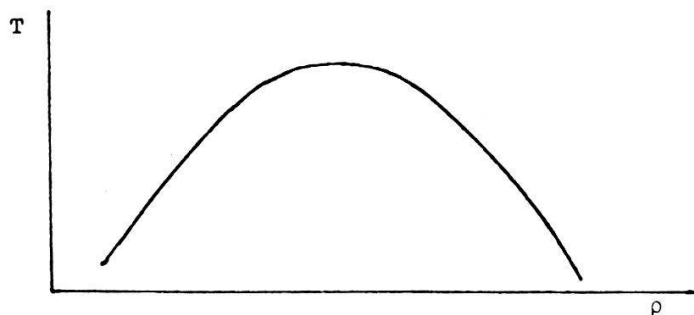


Figure 2

The maximum of the graph of the spinodal curve is the critical point (ρ_c, T_c) , the branch to the left is the projection of the maxima and the branch to the right that of the minima. The corresponding projection onto $\{(p, T)\}$ gives the cusp

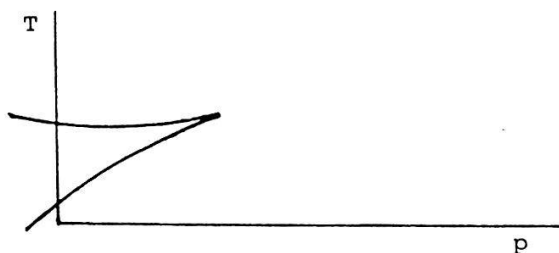


Figure 3

The maximum of the graph corresponds to the critical point, the branch to the left to the projection of the minima and that to the right of the maxima. It is easy to see from the Figures 1, 2 and 3, that the map from the interior of the spinodal curve to the interior of the cusp, defined by

$$(\rho, T) \mapsto (T, \phi(\rho, T))$$

is a diffeomorphism. However, if we consider this map g as a map $N_F \rightarrow \mathbb{R}_+^2$; $(\rho, T) \mapsto (T, \phi(\rho, T))$, then the inverse image of the interior of the cusp is the

⁷⁾ This means that $\pi_A|_l: l \rightarrow \mathcal{E}_T \oplus \mathcal{F}'$ is singular and accordingly that the van der Waals fluid possesses phase transitions of the first kind.

interior of the outer curve in Fig. 4

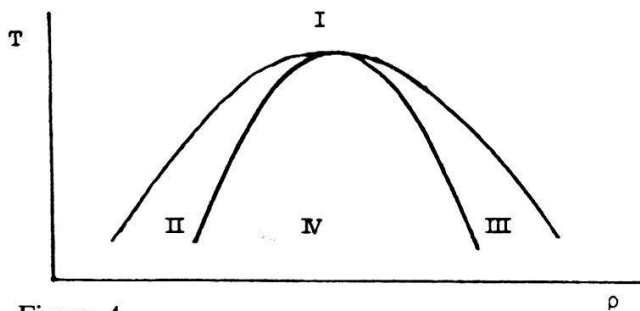


Figure 4

where the inner curve is the spinodal curve. Denote by g_1, g_2, g_3 and g_4 the restrictions of g to the domains I, II, III and IV in Fig. 4. By inspection one can then easily convince oneself that the following proposition holds.

Proposition. g_1 is a diffeomorphism from I to the domain outside the cusp; g_2, g_3 and g_4 are diffeomorphisms from the domains II, III and IV respectively to the interior of the cusp.

The functions ψ_T can be studied in exactly the same way with the same result.

Proposition. Let $h: N_F \rightarrow \{(T, p)\}; (\rho, T) \mapsto (T, \psi_T(\rho))$ and denote by h_1, h_2, h_3 and h_4 the restriction of h to I, II, III and IV respectively; then, h_1 is a diffeomorphism from I to the domain outside the cusp; and h_2, h_3 and h_4 are diffeomorphisms from the domains II, III and IV to the interior of the cusp.

Notice that the cusp that we now are referring to is the cusp in $\{(T, \mu)\}$, corresponding to the projection of the maxima and minima of ψ_T .

With these results at hand, we are ready to discuss the equations (2)

- (i) for (ρ_1, T) and (ρ_2, T) in I, II, III or IV, the equations (2) read respectively

$$\begin{aligned} g_i(\rho_1, T) &= g_i(\rho_2, T) \quad i = 1, 2, 3, 4. \\ h_i(\rho_1, T) &= h_i(\rho_2, T) \end{aligned}$$

which implies $\rho_1 = \rho_2 \forall T$;

- (ii) for $(\rho_1, T) \in II$ and $(\rho_2, T) \in III$, $(\rho_1, T) \in II$ and $(\rho_2, T) \in IV$, and $(\rho_1, T) \in IV$, and $(\rho_2, T) \in III$ however, we get equations of the form

$$\begin{aligned} g_i(\rho_1, T) &= g_j(\rho_2, T) \\ h_i(\rho_1, T) &= h_j(\rho_2, T) \end{aligned}$$

These equations can be solved for ρ_1 and ρ_2 as functions $\rho_1(T)$ and $\rho_2(T)$ of T . The functions solving the above problem is represented by the broken curves in Fig. 5.

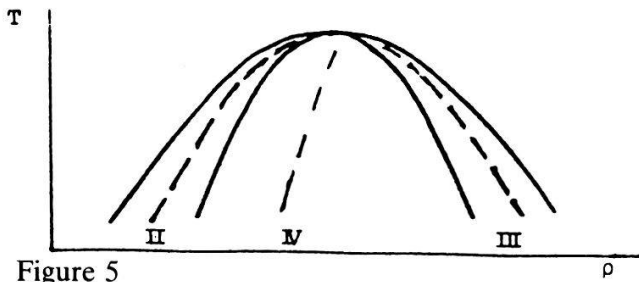


Figure 5

The 'interior' of the curve formed by the branches in II and III will be denoted by \mathcal{M} and the 'exterior' by \mathcal{P} .

The three broken curves are mapped onto the same curve in the cusp by ϕ (and ψ) (Fig. 6).

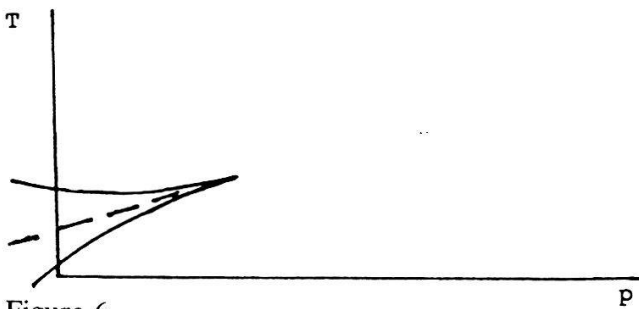


Figure 6

Let the coordinate ρ used throughout be interpreted as the mean mass density, $\rho = M/V$, where $M = \int_{\mathcal{D}} \rho(x) d^3x$ is the mass of the fluid and $V = \int_{\mathcal{D}} d^3x$ the volume it occupies. We are then led naturally to parametrize the solutions of (2) in terms of the points $(\rho, T) \in N'_F$, and can summarize our results so far as follows.

Proposition

- (a) $T_{(\rho, T)}(x) = T$ and $\rho_{(\rho, T)}(x) = \rho$ is a solution of (2) for any $(\rho, T) \in N'_F$;
 (b) for any $(\rho, T) \in \mathcal{M}$, there exists two classes of solutions of the form

$$T_{(\rho, T)}(x) = T$$

$$\rho_{(\rho, T)}(x) = \rho_1(T)\chi_{\Delta}(x) + \rho_2(T)\chi_{\Delta'}(x)$$

where χ_{Δ} and $\chi_{\Delta'}$ are complementary characteristic functions such that $V_1 = \int_{\Delta} d^3x$ and $V_2 = \int_{\Delta'} d^3x$ satisfy

$$\rho_1(T) \frac{V_1}{V} + \rho_2(T) \frac{V_2}{V} = \rho$$

The stability condition

$$\partial_{\rho}^2 f_T > 0$$

is satisfied for $(\rho, T) \in I \cup II \cup III$. This implies that for $(\rho, T) \in \mathcal{P}$, s has only one maximum, i.e. the homogeneous solution a). For $(\rho, T) \in IV$ s has only one maximum also, namely the inhomogeneous solution in b) corresponding to

$\rho_1(T) \in II$ and $\rho_2(T) \in III$. For $(\rho, T) \in (II \cup III) \cap \mathcal{M}$ however, s has two maxima corresponding to the above solution.

Proposition. *The entropy of the inhomogeneous solution (b) is bigger than the entropy of the homogeneous solution.*

Proof. The function of mean entropy density associated with the two solutions are respectively

$$s_1(\rho, T) = -\partial_T f(\rho_2(T), T) \frac{\rho - \rho_1(T)}{\rho_2(T) - \rho_1(T)} - \partial_T f(\rho_1(T), T) \frac{\rho_2(T) - \rho}{\rho_2(T) - \rho_1(T)}$$

$$s_2(\rho, T) = -\partial_T f(\rho, T)$$

A computation of the second derivative of the function $s_{1T} - s_{2T}$ gives

$$\partial_T \partial_\rho^2 f(\rho, T) = -\frac{c_1}{\rho(1 - \beta\rho)} < 0$$

This shows that $(s_{1T} - s_{2T})' : [\rho_1(T); \rho_2(T)] \rightarrow \mathbb{R}$ is a monotonic decreasing function. Together with the fact that $s_{1T} - s_{2T}$ vanishes on the boundary of the interval $[\rho_1(T), \rho_2(T)]$ this implies that $s_{1T} - s_{2T}$ is positive on $\langle \rho_1(T), \rho_2(T) \rangle$.

Accordingly, we have proven the following theorem.

Theorem. *The extrema (a) are absolute maxima for s when $(\rho, T) \in \mathcal{P}$ and relative maxima when $(\rho, T) \in (II \cup III) \cap \mathcal{M}$. The inhomogeneous solutions under (b) with $\rho_1(T) \in II$ and $\rho_2(T) \in III$ are absolute maxima when $(\rho, T) \in \mathcal{M}$.*

Definition. The absolute maxima of s are the equilibrium states; the relative minima are called metastable states.

The thermodynamic free energy function is defined by

$$F(M, V, T) = V f^E\left(T, \frac{M}{V}\right)$$

where

$$f^E(\rho, T) = \begin{cases} f(\rho_1(T), T) \frac{\rho_1(T) - \rho}{\rho_2(T) - \rho_1(T)} + f(\rho_2(T), T) \frac{\rho - \rho_2(T)}{\rho_2(T) - \rho_1(T)}, & (\rho, T) \in \mathcal{M} \\ f(\rho, T), & (\rho, T) \in \mathcal{P} \end{cases}$$

which is easily verified to satisfy the postulates of thermostatics.

The free energy function is once differentiable, i.e. the second derivatives are discontinuous on the coexistence manifold which separates the open submanifolds corresponding to homogeneous and inhomogeneous equilibrium states⁸⁾. The

⁸⁾ This means that L is a C^0 submanifold of E .

coexistence submanifold is thus 2-dimensional. Moreover, it is divided in two by a one-dimensional submanifold, the critical submanifold. If the system is undergoing a process described by a curve crossing first one and then the other of the two parts of the coexistence submanifold it is said to undergo a phase transition of the first kind.

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