EQUILIBRIUM AND METASTABLE STATES OF CLASSICAL SYSTEMS

G.L. Sewell
Department of Physics
Queen Mary College

Mile End Road
London E.1.

The object of this note is to formulate a characterisation of both equilibrium and metastable states of classical systems in terms of certain global and local stability conditions. It will be found that, according to this characterisation, a class of systems with appropriately weakly tempered or long range forces can support metastable states. This result may be regarded as complementary to that of Lanford and Ruelle [1], concerning the absence of metastable states in systems with suitably strongly tempered forces. A preliminary version of the contents of the present note is to be found in Ref. [2].

We shall restrict our formulation here to classical lattice systems: hard-core continuous systems may be similarly formulated within the scheme of Ref. [3].

Let Σ be an assembly of identical, mutually interacting particles on a lattice $T = Z^d$, each site of which is occupiable by at most one particle. The states and forces in Σ may be specified within the framework of Ref. [4]. Accordingly, we represent a particle configuration for Σ by a subset x of T, consisting of the occupied sites. The family X of all subsets of T thus corresponds to a phase space for Σ. For $t \in T$, we define the cylinder set $\sigma_t = \{x \in X \mid t \in x\}$, and equip X with the topology generated by $\{\sigma_t, \; X \setminus \sigma_t \mid t \in T\}$, thereby rendering X compact. We define Y to be the subspace of X whose elements are finite point subsets of T; and we define the state space, Ω, for Σ to be the set of all Radon probability measures on X. Space translations may be represented in X, Y, Ω in obvious fashion. We denote by Ω_T the set of translationally invariant states of Σ.

Let A be the set of all finite point subsets of T. For each $\alpha \in A$, we denote $T \setminus \alpha$ by α_c. We define an equivalence relation $\mathcal{R}(\alpha)$ in X by specifying that $x \mathcal{R}(\alpha) x'$ means that $x \cap \alpha = x' \cap \alpha$; and define $X_\alpha =$

$X/\mathcal{R}(\alpha)$. Thus, each element x_α of X_α is a cylindrical set in X which corresponds to a unique particle configuration in α. We define $\mathcal{B}(\alpha_c)$ to be the σ- algebra generated by the family of cylindrical sets $\{x_{\alpha'} \in X_{\alpha'} | A \ni \alpha' \subset \alpha_c\}$. We denote the restriction of $\omega (\in \Omega)$ to $\mathcal{B}(\alpha_c)$ by ω_{α_c}. If g is a semi-bounded Borel function from X into the extended real line, we denote by $E_\omega(g/\alpha_c)$ the conditional expectation of g with respect to $\mathcal{B}(\alpha_c)$ for the state ω. If χ_B is the characteristic function for a Borel set B in X, we denote $E_\omega(\chi_B/\alpha_c)$ by $\omega(B/\alpha_c)$.

Let $\mathcal{J}$ be the set of continuous, translationally invariant functions ϕ on Y, such that $\phi(\emptyset) = 0$; and let $\|\cdot\|$ and $\|\cdot\|_1$ be the norms on $\mathcal{J}$ defined by the equations

$$\|\phi\| \equiv \sum_{0 \in y} \frac{|\phi(y)|}{N(y)} \quad ; \|\phi\|_1 \equiv \sum_{0 \in y} |\phi(y)| , \tag{1}$$

where N(y) is the number of sites in y. We define Φ (resp. Φ_1) to be the Banach space $\{\phi \in \mathcal{J} | \|\phi\| \text{ (resp. } \|\phi\|_1) < \infty\}$. Thus $\Phi_1 \subset \Phi$. An interaction potential for $\sum$ is taken to be an element ϕ of Φ, with the interpretation that the potential energy of a finite system of particles occupying the point set y is $\sum_{y' \subset y} \phi(y')$. It follows from the definition of Φ that such interactions are both stable and tempered. It may be generally assumed that the chemical potential μ ($\in$ R) is absorbed into ϕ , i.e.

$$\phi(y) = \phi'(y) - \mu\, \delta_{1, N(y)} \quad , \tag{2}$$

where ϕ' ($\in \Phi$) is independent of μ .

For each $\phi \in \Phi$, we define a real valued function H_α^ϕ on X, representing the energy of interaction between particles in α, by the formula

$$H_\alpha^\phi(x) = \sum_{y \subset x} \phi(y) . \tag{3}$$

We define Φ_2 to be the set of elements ϕ of Φ such that, for each $\alpha \in$ A, there exists a lower-bounded Borel function $\tilde{H}_\alpha^\phi$: $X \to R \cup \{\infty\}$ representing the energy of interaction of the particles in α both with one another and with those in α_c , as specified by the following conditions.

$$\text{(a)} \quad \tilde{H}_\alpha^\phi(x \cap a) - \tilde{H}_\alpha^\phi(x' \cap a) = \Bigg[\sum_{y \subset x \cap a;\ y \cap \alpha \neq \emptyset} - \sum_{y \subset x' \cap a;\ y \cap \alpha \neq \emptyset}\Bigg] \phi(y)$$

$$\forall\, A \ni a \supset \alpha, \ x \cap \alpha_c = x' \cap \alpha_c \tag{4}$$

(b) $\tilde{H}^{\phi}_{\alpha}(x) = \lim_{a \to \infty} \tilde{H}^{\phi}_{\alpha}(x \cap a) \ \forall \ x \in X$, (5)
the limit being taken over any increasing absorbing sequence of finite point subsets of T.

(c) For each $x_c \subset \alpha_c$, $\inf_{x \cap \alpha_c = x_c} \tilde{H}^{\phi}_{\alpha}(x) < \infty$.

The conditions (a) - (c) specify $\tilde{H}^{\phi}_{\alpha}$ to within a class of functions which differ from one another by bounded $\mathcal{B}(\alpha_c)$ - measurable functions on X. It may easily be seen that the theory which follows is independent of the choice of $\tilde{H}^{\phi}_{\alpha}$ from this class. It may easily be verified that $\Phi \supset \Phi_2 \supsetneq \Phi_1$.

We define the (global) free energy density functional $f^{\phi}_{\theta} : \Omega_T \to R$, corresponding to the interaction potential ϕ ($\in \Phi$) and temperature θ ($\in R_+$) by the formula (cf [4])

$$f^{\phi}_{\theta}(\omega) = \lim_{\alpha \to \infty} \frac{1}{N(\alpha)} \left[\int H^{\phi}_{\alpha} \, d\omega + k\theta \sum_{x_\alpha \in X_\alpha} \omega(x_\alpha) \ln \omega(x_\alpha) \right], \tag{6}$$

where k is Boltzmann's constant and the limit is taken in Fisher's sense. For $\phi \in \Phi_2$, $\theta \in R_+$ and $\alpha \in A$, we define the conditional free energy functional $F^{\phi}_{\theta,\cdot}(\alpha/\alpha_c)$ on Ω by the equation

$$F^{\phi}_{\theta,\omega}(\alpha/\alpha_c) = \int d\omega_{\alpha_c} \left[E_{\omega}(\tilde{H}^{\phi}_{\alpha}/\alpha_c) + k\theta \sum_{x_\alpha \in X_\alpha} \omega(x_\alpha/\alpha_c) \ln \omega(x_\alpha/\alpha_c) \right]. \tag{7}$$

Thus, $F^{\phi}_{\theta,\omega}(\alpha/\alpha_c)$ corresponds to the free energy of the 'open' system of particles in α, interacting via the potential ϕ both with one another and with the particles in α_c.

<u>Definition 1</u>. We define $K_L(\theta, \phi)$, the set of locally stable states of Σ, corresponding to the interaction ϕ ($\in \Phi_2$) and temperature θ, to consist of those states ω such that, if $\alpha \in A$ and $\omega' \in \Omega$, with

$\omega'_{\alpha_c} = \omega_{\alpha_c}$, then $F^{\phi}_{\theta,\omega}(\alpha/\alpha_c) \leq F^{\phi}_{\theta,\omega'}(\alpha/\alpha_c)$.

<u>Note</u>. Our local stability conditions are equivalent to the Dobrushin-Lanford - Ruelle (D L R) conditions [1,5], as generalised from Φ_1 to Φ_2 - class interactions. However, for our purposes it is essential that $K_L(\theta, \phi)$ be regarded as the set of locally stable states, whereas in Refs. [1, 5] the D L R conditions were taken to define equilibrium states.

Definition 2. Let X^0 be a closed subspace of X, which is stable under space translations, and let Ω^0 (resp. Ω^0_T) $= \{ \omega \in \Omega$ (resp. Ω_T) $|$ supp $\omega \subset X^0 \}$.

(i) Then we define $K_G(\theta, \phi)$ (resp $K^0_G(\theta, \phi)$), the set of globally stable (resp. globally X^0 - stable) translationally invariant states of Σ, corresponding to the interaction ϕ and temperature θ, to consist of those elements ω of Ω_T (resp. Ω^0_T) which absolutely minimise f^ϕ_θ (resp. $f^\phi_\theta | \Omega^0_T$).

(ii) We define the thermodynamic functions P, P^0, from $R_+ \times R$ into R, by the formulae

$$P(\theta,\mu) = -(k\theta)^{-1} \inf_{\omega\in\Omega_T} f^\phi_\theta(\omega) \;;\; P^0(\theta,\mu) = -(k\theta)^{-1} \inf_{\omega\in\Omega^0_T} f^\phi_\theta(\omega), \quad (8)$$

where ϕ is assumed to be expressed in terms of the chemical potential μ according to equation (2). Thus, P represents the pressure of Σ and P^0 represents its pressure when constrained to the reduced phase space X^0.

Note. Since, as noted above, $K_L(\theta, \phi)$ consists of the states which satisfy the D L R conditions, it follows from Ref [1: Theorem 3.2] and Defs. 1, 2 (i) that $K_G(\theta, \phi) = K_L(\theta, \phi) \cap \Omega_T$ if $\phi \in \Phi_1$. However this is not generally true for $\phi \in \Phi \setminus \Phi_1$, as the following example shows.

Example. Let ϕ' be a non-positive-valued element of $\Phi \setminus \Phi_1$. Then it follows from equations (1), (2), (4), (5), together with our definitions of Φ, Φ_1 and Φ_2, that $\phi \in \Phi_2$, with

$$\tilde{H}^\phi_\alpha(x) = -\sum_{y\cap\alpha_c \subset x\cap\alpha_c;\; y\not\subset x} \phi(y). \quad (9)$$

Let σ be the pure state corresponding to the configuration x^σ in which all sites are occupied; and let σ' be an arbitrary state such that $\sigma'_{\alpha_c} = \sigma_{\alpha_c}$. Then it follows from equations (1) and (9) that $E_{\sigma'}(\tilde{H}^\phi_\alpha / \alpha_c) = 0$ if $\sigma' = \sigma$ and $= \infty$ otherwise. Hence, by equation (7) and Def. 1, σ is locally stable for all values of θ and μ. On the other hand, it follows from equations (2), (6) and (7) that, for sufficiently large values of $-\mu$, the global free energy density of σ exceeds that of the state in which all sites are unoccupied. Hence, for such values of μ, ω is locally, but not globally, stable. Further (and trivially!), it is always globally $\{x^\sigma\}$ - stable.

This example reveals the possibility that systems with suitable weakly-tempered (i.e. $\Phi \setminus \Phi_1$ - class) forces can support states which are locally, but not globally, stable. Accordingly, we propose the following definitions of equilibrium and metastable states. The motivation for these definitions, as well as their implications, will be discussed below.

Definition 3. (i) We define the set $K_E(\theta, \phi)$ of translationally invariant equilibrium states of Σ, corresponding to (θ, ϕ), to be $K_G(\theta, \phi) \cap K_L(\theta, \phi)$.

(ii) We define the set $K_M^o(\theta, \phi)$ of translationally invariant X^o - metastable states, corresponding to (θ, ϕ), to be $K_L(\theta, \phi) \cap K_G^o(\theta, \phi) \setminus K_G(\theta, \phi)$. Thus, in this definition, metastability is associated with some specific reduced phase space X^o.

Comments. We envisage that Def. 3 may lead to a theory of metastable states possessing very long lifetimes and 'good' thermodynamical behaviour, as observed experimentally, for the following reasons.

(1) We conjecture, for want of an adequate kinetic theory, that locally stable states are dynamically stable against perturbations arising from the coupling of Σ to a thermal reservoir. In this case, the $K_M^o(\theta, \phi)$ - class states have infinite lifetimes.

(2) By equation (8), P^o corresponds to the pressure of a system Σ^o, say, with phase space X^o and interaction potential ϕ. Thus, P^o serves to generate the thermodynamical laws for Σ^o, just as P does for Σ. Hence the $K_M^o(\theta, \phi)$ - class states exhibit 'good' thermodynamical behaviour, as generated by P^o.

(3) Suppose that, at temperature θ, the system Σ possesses the following properties, which are realisable in certain models (cf. Conclusion (III) below).

(a) The globally X^o - stable states are metastable or true equilibrium states, according to whether $\mu <$ or $>$ some value $\mu_o(\theta)$; and (b) P^o is analytic in μ in some open neighbourhood of $\mu_o(\theta)$. Then it follows from Defs. 2, 3 that, under these conditions, the pressure function P^o for the X^o - metastable phase is an analytic continuation in μ of the pressure P for the equilibrium phase.

Conclusions (I) By Def. 3(ii) and the note following Def. 1, Σ has no metastable states if $\phi \in \Phi_1$.

(II) On the other hand, the example following that note shows that Σ may support metastable states if $\phi \in \Phi \setminus \Phi_1$.

(III) We have obtained similar results for the physically more interesting case of hard-core continuous systems. In particular, we have shown that the Fisher-Felderhof cluster model [6] has a metastable phase corresponding to a superheated liquid, whose pressure function is a smooth continuation of that of the equilibrium liquid phase. These properties stem from the fact that the model satisfies the conditions specified in the above Comment (3), with X^{o} the space of single cluster configurations.

(IV) By extending the present formalism to mean field theories, we have shown that the Van der Waals fluid model, with infinite range Kac potential, has a metastable phase corresponding to a supercooled gas, whose pressure is an analytic continuation of that for the stable gaseous phase (cf. also [7,8]).

References

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