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From phenomenological thermodynamics to the canonical ensemble: II

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Abstract. A general assumption made in a previous paper is modified by the elimination of the metrical entropy in favour of empirical entropy. Without reference to absolute temperature or metrical entropy, one then arrives at a generic form of the canonical probability in phase in which temperature does not occur. It is argued that this is as it should be if one looks upon the canonical ensemble as merely being the representative of a system in thermal equilibrium with its surroundings. One motivation for this work is to take a view of 'statistical mechanics' which does away with probabilistic notions altogether.

1. Introduction

A previous paper (Buchdahl 1979), hereafter referred to as A, was devoted to an attempt to answer the following question: to what extent can the familiar explicit form of the canonical probability in phase,

$$\phi = \alpha \, \mathrm{e}^{(F-H)/kT}, \tag{1}$$

be deduced, granted merely basic *generic* notions of an appropriate statistical formalism and the overriding demand that the laws of phenomenological thermodynamics be accommodated by it, the validity of these laws being taken as unquestioned. Whilst reference has just been made to 'probability in phase' and to 'statistical formalism', I prefer to think of the use of these terms here only as conventional: they should in the first instance by taken as synonymous with 'normalised measure-density function' and, say, 'phase-mean formalism', respectively. Concomitantly the first of these is simply left uninterpreted, whilst the term 'phase-mean' replaces 'ensemble mean'; it is then seen as a quantity defined by the *prescription* of equation (7) of A and reference to ensembles is thus also eliminated. The avoidance of all reference to probabilistic connotations (see A, § 8) harmonises with a view of phenomenological thermodynamics which I have expressed elsewhere (Buchdahl 1981), namely, that it functions as a metatheory, the primary function of which is to act as a selection principle for 'mechanical theories of heat'.

Setting conceptual questions aside, I return to the substance of A, knowledge of the content of which will be taken for granted so that undue repetition may be avoided. By the same token it will be convenient to retain the language used in A rather than that advocated above; if desired, a translation can easily be effected. Granted the rules A(4), it was argued previously that the function w of which the metrical entropy

S was to be the ensemble mean must be determined by the ensemble $\mathbf{K}$ as a whole; and since ϕ fully characterises $\mathbf{K}$ and no other 'collective' phase function is available, one is led to the assumption (B): *w depends upon the phase through ϕ alone.* Taking the full content of the second law into account, it was possible to conclude that

$$\phi = \alpha(S)\, e^{(F-H)/Tk(S)}, \tag{2}$$

where $\alpha(S)$ and $k(S)$ are functions of S alone, subject to the mutual relation $S\mathrm{d}(k^{-1}) - \mathrm{d}(\ln\alpha) = 0$, $k(S)$ itself remaining unknown. (In this context, the mutual diathermic equilibrium of distinct systems K_A and K_B in diathermic contact with the same thermostat—after the fashion of § 6 of A—is, of course, not contemplated; see also § 4 below.)

It was argued in § 7 of A that the appearance of $k(S)$ was tantamount to the 'spontaneous' appearance of an empirical entropy function in the formalism, and that in the first instance some (unspecified) empirical entropy s should appear in place of the metrical entropy S; but that it was not clear how the appearance of S and T in the argument leading to an appropriate form of ϕ might be avoided altogether, if, indeed, it could be avoided at all. The present note addresses itself to the resolution of the unsatisfactory, somewhat confused, state of affairs just outlined.

2. Remarks on the idea of the canonical ensemble

In phenomenological equilibrium thermodynamics a (closed standard) system K in thermal equilibrium with its surroundings $\bar{K}$ occupies a central position, its quasistatic behaviour being governed by the pivotal relation†

$$T\,\mathrm{d}S = \mathrm{d}Q := \mathrm{d}U + \sum_{i=1}^{n-1} P_i\,\mathrm{d}x_i. \tag{3}$$

Correspondingly, in the statistical theory an equally prominent position is occupied by the ensemble representing such a system, that is, by the canonical ensemble. There is room here, however, for a certain ambiguity. I understand a canonical ensemble to be the representative of a system in equilibrium with a (time-independent) heat reservoir; cf Tolman (1938). There is here no mention of temperature, absolute or empirical. Some authors, however, more or less explicitly specify the temperature T of the reservoir; e.g. Pathria (1972). What lies behind this difference is this: only when the temperature is *not* mentioned does the canonical ensemble not presuppose the zeroth law, i.e. the transitivity of the relation of mutual thermal equilibrium of pairs of systems. It suffices to know merely that thermal contact with a reservoir imposes one condition upon the values of the coordinates of K and $\bar{K}$ jointly to give preference to the view that the canonical distribution should in the first instance make no reference to temperature at all. A corresponding situation exists in the phenomenological theory when one prefers the view that the second, first and zeroth laws should be introduced in turn in that order rather than in their traditional order; see Buchdahl (1975). In particular, without drawing upon the zeroth law, one can still infer that there exist functions θ and s of the coordinates of K such that

$$\mathrm{d}Q = \theta\,\mathrm{d}s. \tag{4}$$

† When an 'equation' A = B constitutes a defining relation for A or B it is written A := B and A =: B, respectively.

Consistency demands that to achieve the purpose of A one should initially set out to accommodate (4) rather than (3), if one is to deal appropriately with the consequences of equilibrium between one system and *one* other system.

3. The empirical Helmholtz function $\mathscr{F}$

In A it was necessary to appeal to the minimality of the Helmholtz function F ($:= U - TS$) in equilibrium. Now, however, one has to manage without introducing T so that F is no longer available. To overcome this hiatus, suppose that some particular empirical entropy function s has been chosen so that the functions θ and s are both known. Amongst the coordinates x of K there is one non-deformation coordinate, x_n, say. (In A this was taken to be T, but, of course, that is not to be done here.) As a matter of convenience, go over to a new non-deformation coordinate, taking this to be s. Should θ happen to be independent of s, one goes over to another empirical entropy $\bar{s}$ which is any good, monotonically increasing function of s.

Now contemplate the function

$$\mathscr{F} := U - \theta s, \tag{5}$$

which, as a matter of convention, may be called the 'empirical Helmholtz function'. Then, bearing (4) in mind,

$$\mathrm{d}\mathscr{F} = -\mathrm{d}W - s\ \mathrm{d}\theta. \tag{6}$$

One needs to consider transitions characterised by the constancy of θ. It is whimsical but expedient to call such a transition 'isothetic'. (The condition that θ be not independent of s ensures that in an isothetic transition the deformation coordinates are still freely variable.)

By inspection of (6), the work done by K in a quasistatic isothetic transition is balanced by the decrease of $\mathscr{F}$, just as in the customary isothermal transition it is balanced by the decrease of F. Again, inspection of familiar arguments leading to the usual conclusion that for a transition between given states $\Delta S \geqslant \int \mathrm{d}Q/T$ reveals that equally well

$$\Delta s \geqslant \int \mathrm{d}Q/\theta, \tag{7}$$

and concomitantly stable equilibrium is subject to the conditions

$$\delta\mathscr{F} = 0, \qquad \delta^2\mathscr{F} > 0, \tag{8}$$

granted that all neighbouring unnatural states (Buchdahl 1966) are characterised by fixed values of the deformation coordinates and of θ.

4. The canonical probability in phase

In view of (8), one is now in a position to proceed exactly as in A provided one adopts:

Assumption (B'). *The function* w *of which the empirical entropy* s *is the ensemble mean depends upon the phase through* ϕ *alone.*

This is assumption B except that empirical entropy replaces the metrical entropy. A virtue has been made out of necessity, for what was said in support of assumption B in no way justified its reference to S. On the other hand, one can talk about empirical entropy without any reference to the zeroth or for that matter, the first law.

The direct counterpart to A(25) is here

$$\int \{[H-\theta(\phi w)']\delta\phi + \theta\phi\delta_x w\}\,\mathrm{d}\Gamma = 0. \tag{9}$$

Thereafter everything goes through as before in §§ 5 and 4 of A, save for the formal change of replacing T by θ and S by s everywhere. One therefore ends up with the result

$$\phi = \alpha(s)\,\mathrm{e}^{(\mathscr{F}-H)/\theta k(s)}, \tag{10}$$

where $k(s)$ is an unknown function of s and

$$\mathrm{d}(\ln\alpha)/\mathrm{d}s = s\,\mathrm{d}(k^{-1})/\mathrm{d}s. \tag{11}$$

By means of (11), equation (10) may be rewritten as

$$\phi = \alpha_1 \exp\left(\frac{U-H}{k(s)\theta} - \int\frac{\mathrm{d}s}{k(s)}\right), \tag{12}$$

where α_1 is a (redundant) constant of integration. Equation (12) has exactly the same generic form as A(39): but this time the argument which leads up to it makes no reference to S or T.

To take (12) into the usual form of the canonical probability in phase, one must of course bring in the zeroth law. In effect, one can then set $\theta = T$ and having thus returned to A(29) it only remains to demonstrate the constancy of $k(s)$, say by the method of § 6 of A.

It should be remarked that no reference to Liouville's theorem has been made. One can, of course, verify in retrospect that ϕ satisfies it.

5. Concluding remarks

An unsatisfactory aspect of assumption B, namely its reference to metrical, rather than empirical, entropy has been eliminated. To this extent the argument leading *from* the phenomenological theory *to* the canonical ensemble is made more secure. To achieve such greater security is no idle aim, bearing in mind the purpose of A as outlined in § 1 above. It may be added that the ascription of a metatheoretic function to the phenomenological theory and the adoption of a prescriptive, non-probabilistic stance which goes with it are generally speaking not contemplated when the relationship between the parameters of a system regarded as mechanical and the parameters of the same system regarded as thermodynamic is examined; see, for example, Lavis (1977). At any rate, the path to the canonical ensemble here pursued seems much to be preferred to the kind of argument advanced for instance by Lindsay and Margenau (1957).

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