

“Complementarity” between Energy and Temperature

Jens Lindhard

Institute of Physics, University of Aarhus
Aarhus, Denmark

Contents

Abstract	99
1. Introduction	99
2. The assertion of Rosenfeld	101
3. Measurements of canonical energy distribution	102
3.1. Entropy change and microcanonical width σ_m	104
4. Temperature determined from energy measurements	105
5. Indeterminacy in T for microcanonical ensemble	107
6. General fluctuation	107
7. Particle number and grand potential	109
8. The question of pressure and volume	110
References	111
Discussion	112

Abstract

Niels Bohr's general conception of “complementarity” between energy and temperature was previously taken up quantitatively only by L. Rosenfeld. In the present chapter it is attempted to reconsider the problem. A detailed discussion is made on statistical equilibria, primarily canonical and microcanonical ensembles, as well as their connection to measurements and fluctuations of energy and temperature. In particular, by formal methods and by direct inspection it is shown how a temperature distribution is obtained for an energy fixation. An “uncertainty” relation is obtained for energy and temperature, of a somewhat different kind than the uncertainty relations in quantum theory. A similar relation is found to connect particle number and chemical potential. But the quantities pressure and volume do not show this behaviour, because pressure, for fixed volume, has no fluctuations in an equilibrium ensemble.

1. Introduction

The concept of complementarity was introduced by Niels Bohr in his analysis of the salient features of quantum phenomena. But within physics he also used it when comparing classical mechanics with thermodynamics. He wrote only little about it.

Still, in his Faraday lecture (Bohr 1932) one whole page is devoted to the mechanical-thermodynamic complementarity; it is formulated in rather general terms and written less lucidly than he usually did.

Many of you will have heard him emphasize the superiority of Gibbs' conceptions as compared to those of Boltzmann. He said that Gibbs' ensemble was the proper kind of theoretical approach, at first extremely abstract, but then when one brought together two ensembles with the same modulus, they turned out to reproduce exactly experimental findings and the basic concept of temperature equilibrium. Heisenberg tells vividly about this in an interview from 1963, quoted in Niels Bohr, *Collected Works*, Vol. 6 (Kalckar 1985 pp. 324–326).

Heisenberg has also attempted to formulate Bohr's views in his memoirs: "Der Teil und das Ganze" (Heisenberg 1969), where he reconstructs a discussion with Bohr, Kramers and Klein. Heisenberg leaves the impression—an impression that many others have had from Bohr—that a "complementary" conception of the relation between mechanics and thermodynamics was important to Bohr long before he introduced the concept, and the word, in quantum theory. Heisenberg discusses explicitly the complementarity between energy and temperature for a molecule in a cup of tea. But there is no quantitative discussion.

The only quantitative attempt that I know of was published by Rosenfeld (1962). I shall come back to that below, since it will be the starting point of my analysis.

A discussion of complementarity between energy and temperature should have several implications. The quantitative aspects of it may possibly be expressed in terms of "uncertainty" relations between energy and temperature, as will be discussed in the following. But there is also the question of whether energy and temperature belong to different experimental arrangements, and how idealized measurements are performed. Next, we might be able to learn what entropy increases are associated with measurement. This was treated by Szilárd some sixty years ago in his familiar example of a molecule in a box, where a shutter can divide the box in two parts (Szilárd 1929). Szilárd's conclusion about entropy increase in the measuring process was discussed by Bohr in correspondence with Pauli and with Stern (cf. Kalckar 1985 pp. 326–330, 449–456, 467–473). When describing the measuring process in quantum theory, and in later years especially, Niels Bohr emphasized the importance of irreversibility in measurements. The problem of Szilárd is not the subject of the present chapter, however, and it will only be touched upon briefly.

It should be added that a discussion of complementarity between energy and temperature and of their measurement, all within classical physics, may be a useful background for the understanding of quantal phenomena. In point of fact, Heisenberg (1969) concludes the above-mentioned discussion by noting the different attitudes of Bohr and Einstein:

"Wir konnten nun gut verstehen, warum für Niels der grundsätzliche Unterschied zwischen den statistischen Gesetzen der Wärmelehre und denen der Quantenmechanik viel weniger bedeutsam war als für Einstein. Niels empfand die Komplementarität als einen zentralen Zug der Naturbeschreibung, der in der alten statistischen Wärmelehre, insbesondere in der durch Gibbs gegebenen Fassung, schon immer vorhanden, aber

nicht genügend beachtet worden war; während Einstein immer noch von der Vorstellungswelt der Newtonschen Mechanik oder der Maxwellschen Feldtheorie ausging und die komplementären Züge in der statistische Thermodynamik gar nicht bemerkt hatte.”

2. The assertion of Rosenfeld

Consider the simplest thermodynamic system, where only one parameter is varied, i.e. within classical thermodynamics we are concerned with energy E and entropy S , and with the derived quantities, temperature T and specific heat C ,

$$E = E(S), \quad dE = T dS, \quad \frac{dE}{dT} = C, \quad (2.1)$$

where the specific heat $C = C(T)$ can be used to characterize the properties of the system.

For a system of this kind, L. Rosenfeld (1962) applied fluctuation theory of equilibrium statistical mechanics and obtained the following connection between the fluctuations of energy and temperature:

$$\delta E \cdot \delta T = kT^2, \quad \text{or} \quad \delta E \cdot \delta \beta = 1, \quad \beta = \frac{1}{kT}, \quad (2.2)$$

where the fluctuations are given by the averages

$$(\delta E)^2 = \overline{(E - \bar{E})^2}, \quad (\delta T)^2 = \overline{(T - \bar{T})^2}. \quad (2.3)$$

Rosenfeld emphasizes that, whereas δE depends on the size of the system, the result (2.2) is independent of the size. He says that the reciprocal relationship between energy and temperature is closely analogous to the uncertainty relations in quantum theory.

Now, there appears to be something quite strange in this result of Rosenfeld. In fact, the canonical ensemble one conceives as having an exact temperature T , and a finite energy fluctuation, in disagreement with eq. (2.2). Similarly, if we have a system with vanishing δE it is hard to imagine that the fluctuation δT is unlimited large.

At this stage it is proper to introduce the canonical distribution of energy E , for a system with differential phase volume, or density of states, $\rho(E) dE$. The total differential probability is

$$W(E) dE = P(E) \rho(E) dE = K \exp\left(-\frac{E}{kT}\right) \rho(E) dE, \quad (2.4)$$

where T is the temperature, and where the normalization constant K is associated with the free energy, $\log K = F/kT$.

In the following, I use mostly Gaussian approximations, since they are sufficiently accurate for my purpose. We can expand the density $\rho(E)$ around the point

of most probable energy, E_p ,

$$\rho(E) \cong \rho(E_p) \exp\left[\frac{E - E_p}{kT} - \frac{(E - E_p)^2}{2\sigma_c^2}\right], \quad (2.5)$$

where E_p and σ_c are determined by, respectively,

$$\frac{d}{dE_p} \log \rho(E_p) = \frac{1}{kT}, \quad \text{and} \quad \frac{d^2}{dE_p^2} \log \rho(E_p) = -\frac{1}{\sigma_c^2}. \quad (2.6)$$

It follows that, in this approximation, eq. (2.4) becomes

$$W(E) = \frac{1}{\sigma_c \sqrt{2\pi}} \exp\left[-\frac{(E - E_p)^2}{2\sigma_c^2}\right], \quad (2.7)$$

and the energy square fluctuation is determined by the specific heat according to eq. (2.6),

$$\sigma_c^2 = kT^2 C. \quad (2.8)$$

How Rosenfeld derived eq. (2.2) is not completely clear. But he refers to the discussion of fluctuations by Landau and Lifshitz (1958). They consider a small subsystem and derive fluctuations, like Einstein, by connecting probability to entropy and for the remainder use classical thermodynamics.

Now, if in the above canonical fluctuation (2.8) we write $(\delta E)^2 = \sigma_c^2$, and furthermore introduce a formal temperature, changing with E such that

$$\delta T = \delta E / \frac{dE}{dT} = \delta E / C,$$

we might replace one δE by δT and arrive at Rosenfeld's formula (2.2). But this replacement contains two errors. First, the temperature does not fluctuate in eq. (2.4) because it is a canonical distribution; second, if we let the formal temperature fluctuate with E , the fluctuations δT and δE in eq. (2.2) are not independent, so that it is not an uncertainty relation, where the fluctuations must be independent.

In order to clarify the situation, I shall proceed in small steps, looking first at the simplest cases, explaining each "Gedankenexperiment" and the connected formalism.

3. Measurements of canonical energy distribution

Canonical and microcanonical ensembles are distributions where complete equilibrium has been obtained within the available phase space, and where thus time does not exist. One can compare equilibria before and after a process has occurred,

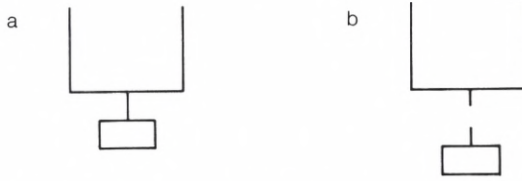


Fig. 1. (a) Canonical equilibrium; (b) isolation of a small system.

however. This is quite like the assumptions in basic thermodynamics. My task is to look into the concepts of energy and temperature, as well as their measurement, for equilibrium ensembles.

The canonical ensemble is an idealized case, like a plane wave in quantum theory. Within Gedankenexperiments, it may be realized with arbitrary accuracy as the phase space distribution of a small system in equilibrium with a very large one. Together, the two form a total system which is isolated and may be supposed to be microcanonical, i.e. with a rather sharply defined total energy. Again, the isolated system is an idealized concept: we can isolate with high perfection, but not completely.

Let me compare one aspect of measurements in quantum theory and in statistical ensembles. If, for the quantal case as well as for the canonical distribution, one desires to measure probability density at a single point (\bar{r}_0 or E_m), the fixation of the variable in question requires a drastic intervention and a change of the physical system. This is the type of measurement with which we are concerned for the present. But it should not be forgotten that there are also less drastic measurements, where *averages* of the probability distributions are measured (e.g. average energy), and where the system itself may be left in an essentially unchanged state; in the case of wave functions it could be elastic scattering of an external particle on the system (form factor), and for canonical distributions an example is afforded by measurements of pressure, as we shall see in section 8.

With this in mind we see that the obvious way in which to measure the canonical distribution in energy for the small system is, first, to isolate it from the large system, as illustrated in fig. 1. The small system then becomes a microcanonical

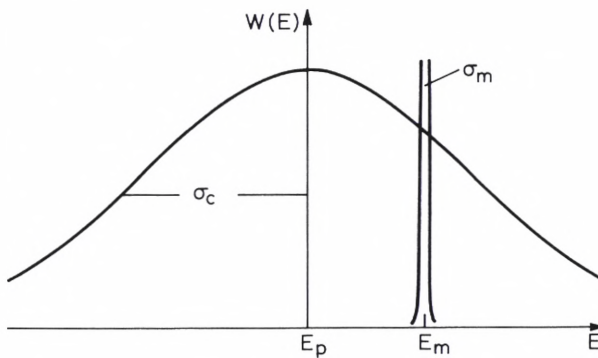


Fig. 2. Microcanonical ensemble after measurement in a canonical ensemble.

system, which is characterized by an energy centre E_m , and a very small width, $\sigma_m \ll \sigma_c$. Second, the value of E_m is measured. The outcome of the experiment will then be some value of E_m , in the neighbourhood of E_p (cf. fig. 2). The distribution of E_m must be given by the Gaussian (2.7), where E is to be replaced by E_m and where the width is the canonical one, σ_c . This is like any proper probability distribution, such as a stationary wave function in space, where $|\varphi(\bar{r})|^2$ gives the probability density for the coordinate \bar{r} , when we make a measurement.

We can therefore state that the uncertainties are

$$(\delta E)^2 = \sigma_c^2 = kT^2C, \quad \delta T = 0, \text{ canonical ensemble.} \quad (3.1)$$

3.1. Entropy change and microcanonical width σ_m

In the above arises, as a side issue, the question of entropy change by reduction from a canonical to a microcanonical ensemble. It is necessary to show that, for the present purposes, this entropy change is not of importance, and neither is the magnitude of the microcanonical width σ_m . But they are of interest in a study of the measuring process itself.

For simplicity, I suppose that a microcanonical ensemble is Gaussian, or

$$W_m(E) = P_m(E) \rho(E) = \frac{1}{\sigma_m \sqrt{2\pi}} \exp \left[-\frac{(E - E_m)^2}{2\sigma_m^2} \right]. \quad (3.2)$$

Let us here consider only the change in entropy due to the change of width of the distribution; the consequence of E_m being different from E_p is dealt with in section 5. We therefore assume that $E_m = E_p$, and since the entropy is given by

$$S = -k \int dE W(E) \log P(E), \quad (3.3)$$

the entropy change becomes

$$\delta S_{\text{width}} = S_m - S_c = -k \log \frac{\sigma_c}{\sigma_m} + \frac{1}{2}k \left(1 - \frac{\sigma_m^2}{\sigma_c^2} \right), \quad (3.4)$$

the formula being valid for any value of σ_m , with a maximum equal to zero for $\sigma_m = \sigma_c$. For $\sigma_m \ll \sigma_c$, it can be seen that eq. (3.4) corresponds to simple expectations, because the available volume in phase space has been reduced by a factor σ_m/σ_c , and $\delta S_{\text{width}}/k$ is essentially the logarithm of that factor.

The total entropy change is slightly different from eq. (3.4) because, as follows from eq. (5.1), the shift of E_m with respect to E_p gives on the average a small change $-k/2$, so that the total entropy change becomes, since $\sigma_m \ll \sigma_c$

$$\delta S \approx -k \log \frac{\sigma_c}{\sigma_m} = -\frac{k}{2} \log \frac{3N}{2} - k \log \frac{kT}{\sigma_m}, \quad (3.5)$$

where, for definiteness, the value of σ_c for a free gas of N particles has been introduced. It should also be noted that the energy shift $E_m - E_p$ gives rise to an exchange of entropy $\sim \pm kN^{1/2}$ between the small system and the large one.

It follows then that, for large N , both of the terms on the right-hand side of eq. (3.5) are negligible compared to the leading entropy terms, proportional to N , or to $N^{1/2}$. By narrowing down one degree of freedom (energy), we cannot essentially affect the entropy of a system with many effective degrees of freedom. In this connection it is noteworthy that, because of the logarithm, an upper limit of as little as $\sim 100 k$ exists for the value of $|\delta S|$ for any system whatever.

But there is another aspect of the moderate entropy decrease. If we have to suppose, with Szilárd (1929), that the entropy of the measuring apparatus plus system can never decrease, the total process of isolation and measurement must involve an entropy increase at least compensating for the decrease (3.5). This interesting question, however, is outside the main purpose in the present discussion.

4. Temperature determined from energy measurements

In the other sections I approximate all distributions by Gaussians. In order to make a few rigorous deductions, I shall now use the accurate distributions.

The preceding section was concerned with a familiar situation within problems of statistics. With a known parameter ($\beta = 1/kT$) of the probability distribution, we can observe the various outcomes (E_1, E_2, \dots). There are simple basic rules for probabilities, including a product rule for probabilities of independent events, or successive measurements.

In the further discussion it is important that the canonical distribution has special properties. Suppose that the density $\rho(E)$ is composed of densities of two independent systems, $\rho_1(E_1)$ and $\rho_2(E_2)$. It holds then that the canonical distribution $\exp(-\beta E) \rho(E) dE$ is a product of two distributions, $\exp(-\beta E_1) \rho_1(E_1) dE_1$ and $\exp(-\beta E_2) \rho_2(E_2) dE_2$, where next $E_1 + E_2 = E$. The total density is given by

$$\rho(E) = \int_0^E dE_1 \rho_1(E_1) \rho_2(E - E_1). \quad (4.1)$$

If we now ask for the probability distribution $W_{E,\beta}(E_1)$ of E_1 for given E and β , we observe that the exponential factor $\exp(-\beta E_1 - \beta E_2) = \exp(-\beta E)$ is independent of E_1 , and therefore

$$W_{\beta,E}(E_1) dE_1 = \frac{\rho_1(E_1) \rho_2(E - E_1)}{\rho(E)} dE_1. \quad (4.2)$$

This result is remarkable in that the probability for E_1 is independent of β , so that E_1 has become a redundant variable. It follows that if we make a number of measurements by means of the small system, the only relevant energy is the sum of the measured energies $E = E_1 + E_2 + E_3 + \dots$, together with the formal total density $\rho(E)$, obtained by successive integrations of the type of eq. (4.1). When the

number of measurements goes to infinity, the relative width of the canonical distribution of E tends to zero, and we obtain the limit of classical thermodynamics.

Our central problem consists in the inversion of the above situation (Lindhard 1974): Suppose that we know the results (E_1, E_2, \dots) of one or more measurements, and ask what statement can be made about the unknown parameter (β) of the distribution. To this end we already found a characteristic property of the canonical distribution, in that only the energy sum E and the integrated density $\rho(E)$ are relevant. Our problem is reduced to an inversion of a distribution of the simple type $W_\beta(E) = -K \exp(-\beta E) \rho(E)$. Since this is a normalized mass distribution along the E -axis changing monotonously with β , the corresponding normalized mass distribution along the β -axis becomes

$$\Pi_E(\beta) d\beta = d\beta \frac{\partial}{\partial \beta} \int_0^E dE' W_\beta(E'). \quad (4.3)$$

The result (4.3) is the unique solution of inversion. Thus, it is obvious that the formula has the necessary property of a repeated inversion leading back to the original distribution. It is also easy to show that it is the only possible solution.

If we introduce the canonical distribution in eq. (4.3), we find for the inversion

$$\Pi_E(\beta) d\beta = d\beta \frac{\partial}{\partial \beta} \int_0^E K e^{-\beta E'} \rho(E') dE'. \quad (4.4)$$

In the particular case of a gas of N free particles, simple scaling prevails, and the two distributions are of the same kind, i.e.

$$W_\beta(E) dE = \frac{1}{\Gamma(\frac{3}{2}N)} \beta^{\frac{3}{2}N} e^{-\beta E} E^{\frac{3}{2}N-1} dE, \quad (4.5)$$

$$\Pi_E(\beta) d\beta = \frac{1}{\Gamma(\frac{3}{2}N)} E^{\frac{3}{2}N} e^{-E\beta} \beta^{\frac{3}{2}N-1} d\beta. \quad (4.6)$$

Note that when n measurements are made with a gas of N particles, we replace N by nN in eqs. (4.5) and (4.6), as is seen from the composition rule for densities, eq. (4.1).

By means of the distributions (4.4) or (4.6) we have obtained statements about the unknown parameter β of the heat source, when measurements of total energy E are made. The statements are not unlike usual probability distributions, but their contents are of a more abstract kind. The two distributions may be conceived, however, in another way than to give an estimate of an unknown source parameter. In fact, we have merely a total microcanonical system of energy E , irrespective of the way in which it is achieved. Therefore, eqs. (4.4) and (4.6) also represent the distribution of β , or of temperature, for a microcanonical system.

In eqs. (4.4)–(4.6), it is easy to obtain the Gaussian approximations. In point of fact, if we had started from a Gaussian distribution $W_\beta(E)$ with small relative width, the problem of inversion would have been trivial, and would have had the same results.

5. Indeterminacy in T for microcanonical ensemble

In place of the formal derivation in the preceding section, let us consider the basic and conceptually simple way of determining the temperature of a system, and thereby find the indeterminacy in T . In fact, suppose that we have a very large system with well-defined temperature T , bring the small microcanonical system in contact with it, and demand that there is no essential change by contact. If this is the case, the temperature of the small system was equal to T . This experiment can also be illustrated by fig. 2, where the narrow peak then represents the small system before contact, and the broad Gaussian indicates its subsequent canonical equilibrium.

The measure of the lack of equilibrium by contact must be the magnitude of the irreversible change of entropy. I have already given the change of entropy, δS_{width} , due to the change in width of the distribution [cf. eq. (3.3)]. We can disregard this unavoidable and constant term. Consider therefore the entropy change connected with the shift of the most probable energy from E_m to E_p . There is an energy transfer $E_m - E_p$ to the large system, for which the temperature remains constant. For the small system we can also use classical thermodynamics [eq. (2.1)], but its temperature changes slightly during the process. In all we obtain an entropy change

$$\begin{aligned} \delta S_{\text{shift}} &= \frac{E_m - E_p}{T} + \int_{E_m}^{E_p} \frac{dE'}{T'} \\ &= \frac{E_m - E_p}{T} + \int_{E_m}^{E_p} dE' \left\{ \frac{1}{T} - \frac{T' - T}{T^2} \right\} = \frac{(E_m - E_p)^2}{2CT^2}. \end{aligned} \quad (5.1)$$

It is not surprising that eq. (5.1) corresponds to minus the exponent in the Gaussian (2.7), representing the canonical distribution, because we are concerned with the same process in the opposite direction.

The increase of entropy, eq. (5.1), remains less than $k/2$ when $(E_m - E_p)^2 < \sigma_c^2$, and when this condition is fulfilled there is effective temperature equilibrium with the large system. Since here the change of energy corresponds to a change of temperature, $dE = C dT$, we obtain the following uncertainties for the microcanonical ensemble

$$C^2(\delta T)^2 = \sigma_c^2 = kT^2C, \quad \delta E \approx 0, \text{ microcanonical ensemble.} \quad (5.2)$$

This simple estimate is in agreement with the precise description (4.4), where the distribution of temperature was obtained.

6. General fluctuation

So far, I have merely discussed the two limiting cases of fluctuations, represented by the microcanonical and canonical ensemble. But when we examine these cases, we



Fig. 3. Equilibrium and isolation.

find that it is not difficult to construct intermediate situations too. In fact, suppose that the small system, with heat capacity C , is in equilibrium with another system having heat capacity ξC . If $\xi = 0$, the small system is microcanonical, and if $\xi \rightarrow \infty$ it becomes canonical. The process of measurement, by isolation and subsequent energy determination of the small system, is illustrated in fig. 3 and is quite analogous to the canonical equilibrium in fig. 1.

The combined system is microcanonical with total energy E_{tot} . The density of states is $\rho(E)$ for the small system, and $\rho_0(E_{\text{tot}} - E)$ for the other one. From this we find the probability distribution and make a Gaussian expansion around the most probable energy E_p ,

$$\begin{aligned}
 W(E) &= K \rho_0(E_{\text{tot}} - E) \rho(E) \\
 &\simeq K' \exp\left(-\frac{E}{kT} - \frac{(E - E_p)^2}{2\sigma_c^2 \xi}\right) \exp\left(\frac{E - E_p}{kT} - \frac{(E - E_p)^2}{2\sigma_c^2}\right) \\
 &= \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-\frac{(E - E_p)^2}{2\sigma^2}\right), \tag{6.1}
 \end{aligned}$$

where

$$\sigma^2 = \sigma_c^2 \frac{\xi}{1 + \xi}, \tag{6.2}$$

σ_c being the canonical width [see eq. (2.8)]. This means that the energy fluctuation in equilibrium is somewhat smaller than the canonical one:

$$(\delta E)^2 = \sigma_c^2 \frac{\xi}{1 + \xi}. \tag{6.3}$$

It remains to find the indeterminacy δT in temperature for the equilibrium. But since the total system is microcanonical, with heat capacity $(1 + \xi)C$, we can use the fluctuation eq. (4.2) with the heat capacity changed by a factor $(1 + \xi)$, i.e.

$$C^2 (\delta T)^2 = \sigma_c^2 \frac{1}{1 + \xi}. \tag{6.4}$$

This is the temperature indeterminacy for the total system, and hence also for its subsystems. By a more cursory argument, we can also arrive at eq. (6.4) directly

from the property (6.3) of the small system. In fact, if the result (6.3) for the fluctuation is supposed to arise from an ensemble mixture of a canonical and a microcanonical system, the former must have a probability $\xi/(1 + \xi)$ and the latter therefore a probability $1/(1 + \xi)$. The temperature fluctuation arises from the microcanonical system only, for which it is given by eq. (4.2), and the probability factor $1/(1 + \xi)$ thus leads to eq. (6.4).

Combining eqs. (6.3) and (6.4) we arrive at the general fluctuation formula

$$(\delta E)^2 + C^2(\delta T)^2 = kT^2C, \quad (6.5)$$

for a system with heat capacity C . It is implicitly assumed, because of the Gaussian approximation, that the fluctuations are small in a relative sense. This means that k/C is small, so that the effective number of particles participating is $N_{\text{eff}} \gg 1$.

The result (6.5) was obtained for Gaussian distributions with widths between zero and σ_c , corresponding to the range of possibilities obtainable for systems in equilibrium. If we imagine other distributions $W(E)$, the left-hand side of eq. (6.5) cannot become less; it can only increase. Simple examples are a Gaussian with width greater than σ_c , or a non-Gaussian distribution with a square fluctuation equal to σ_c^2 , where the left-hand side of eq. (6.5) would exceed the right-hand side. We therefore get a more general result when replacing “=” by “ \geq ” in eq. (6.5).

We have hereby obtained a quantitative expression for complementarity between energy and temperature. The result is not quite like the uncertainty relations in quantum theory. In fact, it also follows from eq. (6.5) that if we form the product $\delta E \delta T$ corresponding to Rosenfeld's formula (2.2), it will not have any particular physical significance, being between zero and an upper limit $kT^2/2$, and with inequality sign in eq. (6.5) there is not even an upper limit.

Let me finally exemplify and extend the result (6.5). Consider a gas of N free particles, where $C = 3NkT/2$, and rewrite the resulting equation in the form

$$\frac{(\delta E)^2}{\bar{E}^2} + \frac{(\delta\beta)^2}{\bar{\beta}^2} \geq \frac{2}{3}N,$$

so that it holds for more general probability distributions $W(E)$, as well as for small values of N , where eqs. (4.5) and (4.6) are applicable.

7. Particle number and grand potential

It is natural to ask whether connections similar to those in eq. (6.5) exist for other sets of thermodynamic variables too. An obvious possibility is afforded by the grand canonical ensemble, where the particle number and the chemical potential play similar roles as energy and temperature, respectively. For the grand ensemble the number of particles N becomes a free variable and, in analogy to $\exp(-E/kT)$, there appears a probability factor $\exp(N\mu/kT)$, μ being the chemical potential. The analogy to $\rho(E)$ is a weight factor decreasing with increasing N , for large N . In the

simplest case—a gas of free particles—the weight factor becomes $\lambda^N/N!$, and the probability of N particles is then given by the Poisson distribution, the average number \bar{N} then being proportional to $\exp(\mu/kT)$.

In general, the square fluctuation of the number of particles in the grand ensemble is

$$\sigma_g^2 = kT \frac{\partial}{\partial \mu} \bar{N}. \quad (7.1)$$

One might now, using Gaussian approximations for the distribution, go through the derivations corresponding to sections 2–6. The final result, corresponding to eq. (6.5), is found easily by

$$(\delta N)^2 + \left(\frac{\partial \bar{N}}{\partial \mu} \right)^2 (\delta \mu)^2 = kT \frac{\partial}{\partial \mu} \bar{N}. \quad (7.2)$$

The Gaussian approximations imply again that relative fluctuations, such as $\delta N/\bar{N}$, are small. In the case of a gas of free particles, eq. (7.2) becomes

$$\frac{(\delta N)^2}{\bar{N}^2} + \frac{(\delta \mu)^2}{(kT)^2} = \frac{1}{\bar{N}}. \quad (7.3)$$

For completeness, it should be mentioned that there are two exceptions to the complete analogy with results in the previous sections, both due to the particle number being discrete, in contrast to the energy. They are of no significance when N is large. First, the decrease in entropy δS_{width} , when the grand ensemble is replaced by a definite number of particles, is

$$\delta S_{\text{width}} = -k \log \sigma_g, \quad (7.4)$$

which quantity becomes $-(k/2) \log \bar{N}$, for a gas.

The second exception to the analogy is concerned with the exact inversion $W_\mu(N) \rightarrow W_N(\mu)$, where the attempt to represent a continuum variable (μ) by means of a discrete one (N) introduces a peculiar latitude (cf. Lindhard 1974, §5).

8. The question of pressure and volume

It might seem as if also pressure and volume were a pair of variables which could be of interest in the present context. It should be realized, however, that pressure is quite a peculiar quantity. Since it corresponds to work divided by volume change, it can hardly be well-defined unless the work is performed infinitely slowly. This is because a volume change in a finite time interval contains an ambiguous velocity of a piston, depending on its area, the velocity possibly competing with molecular velocities. The concept of pressure then applies precisely for systems in equilibrium,

like canonical and microcanonical ensembles. Pressure can be measured directly in either ensemble by an adiabatic process. But that process contains an unlimited number of collisions, and if we consider the corresponding work for a given volume change δV , the average work $\overline{\delta W} = \bar{p}\delta V$ will be composed of an unlimited number of equivalent terms and therefore the work will have a vanishing fluctuation. Because pressure depends on the number of collisions, and not on the number of particles in the system, it is without fluctuations, and we have no connection to the present fluctuation problems.

This result is also obtained by closer scrutiny of current estimates of pressure fluctuations of canonical distributions, cf. the review by Münster (1959), Wergeland (1962) and Klein (1960). In such treatments it is explicitly, or implicitly, assumed that there are no pressure fluctuations in a microcanonical ensemble. The fluctuations in pressure are claimed to arise as a consequence of energy fluctuations, and estimated to be $(\delta p/p)^2 = (\delta E/E)^2 = \frac{2}{3}N$ in a canonical gas of N particles. However, when a microcanonical ensemble has no fluctuations in pressure, and a canonical ensemble can be a subsystem of a microcanonical one, the canonical ensemble cannot either have fluctuations, since a measurement of pressure for the canonical subsystem can also be a measurement for the total system. The cited pressure fluctuations therefore do not belong to a direct measurement of pressure for a canonical distribution, but rather to a series of experiments corresponding to figs. 1 and 2, where the system is isolated, after which pressure (and energy) is measured; the resulting pressures will then follow the variation of the energies and acquire their fluctuation.

This discussion shows, again, that it is important to specify clearly the detailed experimental background, when one makes theoretical estimates of some physical quantity belonging to a system in statistical mechanics.

Acknowledgements

In a previous paper, in collaboration with Jørgen Kalckar (Lindhard and Kalckar 1982), the relationship of energy and temperature was treated, and preliminary results were obtained. I am much indebted to Jørgen Kalckar for numerous discussions, and for encouragement and criticism, from which I have profited much. I also wish to express my indebtedness to J.U. Andersen and E. Eilertsen for many critical comments on the manuscript.

I am particularly grateful to Susann Toldi for careful and competent preparation of the paper.

References

- Bohr, N., 1932, Faraday Lecture, in: *J. Chem. Soc. London*, p. 349–384; cf. p. 376–377.
 Heisenberg, W., 1969, *Der Teil und das Ganze* (R. Piper & Co. Verlag, München) ch. 9.
 Kalckar, J. (ed.), 1985, Niels Bohr, *Collected Works*, Vol. 6, *Foundations of Quantum Physics I* (North-Holland, Amsterdam).
 Klein, M.J., 1960, *Physica* **26**, 1073.

- Landau, L.D., and E.M. Lifshitz, 1958, *Statistical Physics* (Pergamon Press, London, New York).
- Lindhard, J., 1974, *Mat.-Fys. Medd. Dan. Vidensk. Selsk.* **30**, No. 1.
- Lindhard, J., and J. Kalckar, 1982, *Fysisk Tidsskrift* **80**, 60.
- Münster, A., 1959, *Handbuch der Physik*, Vol. III/2 (Springer Verlag, Heidelberg) p. 176.
- Rosenfeld, L., 1962, *Proc. Enrico Fermi School of Physics*, Vol. 14 (Academic Press, New York) p. 1.
- Szilárd, L., 1929, *Z. Phys.* **53**, 840.
- Wergeland, H., 1962, in: *Fundamental Problems in Statistical Mechanics*, ed. E.G.D. Cohen (North-Holland, Amsterdam) p. 33.

Discussion, session chairman S. Belyaev

Kubo: You discussed a small system which is in contact with a heat bath. Its distribution of energy is a canonical distribution, determined by the temperature of the bath. So the energy of this system fluctuates, and the fluctuations are given in terms of the bath temperature. The temperature of that small system is something different from the temperature of the heat bath, and you can directly interpret the energy fluctuations as temperature fluctuations. Introducing the heat capacity, you can easily get the result $\Delta E \cdot \Delta T = kT^2$. I think that this is the simplest interpretation of this relation.

Lindhard: This was the Rosenfeld result, with a product $\Delta E \cdot \Delta T$, but that is a case of dependent fluctuations of E and T . It is not at all fluctuations of the kind that are involved in uncertainty relations in quantum mechanics. The two statistical fluctuations ΔE and ΔT have to be independent of each other in order to be of interest.