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Thermodynamics of the Exponential Lattice

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In this note, thermodynamical and statistical-mechanical tratment of the exponential lattice is presented. Especially, it is pointed out that the partition function can be written as a product of harmonic and unharmonic parts. Consideration is also given to the wave propagation through the lattice at finite temperatures.

§ 1. Thermodynamics

The Hamiltonian of a one-dimensional lattice with nearest neighbor interaction is written as

$$\mathcal{H} = \sum_{n=1}^{N} \frac{m}{2} \dot{y}_n^2 + \sum_{n=1}^{N} \phi(r_n) . \tag{1.1}$$

For the exponential lattice, the interaction potential is

$$\phi(r) = \frac{a}{b}\left(e^{-b(r-\sigma)} - 1\right) + a(r-\sigma) . \tag{1.2}$$

The pressure P is the average of the force, or

$$P = -\overline{\frac{d\phi(r)}{dr}} = a\left(\overline{e^{-b(r-\sigma)} - 1}\right) \tag{1.3}$$

and the internal energy E is

$$E = \overline{\mathcal{H}} = \sum_n \frac{m}{2} \overline{\dot{y}_n^2} + \sum_n \overline{\phi(r_n)} \tag{1.4}$$

where

$$\overline{\phi(r)} = \frac{a}{b}\left(\overline{e^{-b(r-\sigma)} - 1}\right) + a(\bar{r} - \sigma)$$

$$= \frac{P}{b} + a(\bar{r} - \sigma) , \qquad (1.5)$$

and in the classical case, the law of equipartition of energy gives

$$\frac{m}{2}\overline{\dot{y}_r^2} = \frac{kT}{2} . \qquad (1.6)$$

Thus we see that the internal energy of the nonlinear lattice is a "linear" function of the temperature T, the presure P, and the length L of the lattice:

$$E = \frac{NkT}{2} + \frac{NP}{2} + a(L - N\sigma) . \qquad (1.7)$$

Let G be the thermodynamic potential, then we have the thermodynamic relations

$$E + PL = \left(\frac{\partial G/T}{\partial\, 1/T}\right)_P , \qquad (1.8)$$

$$L = \left(\frac{\partial G}{\partial P}\right)_T = T\left(\frac{\partial G/T}{\partial P}\right)_T . \qquad (1.9)$$

Therefore if we introduce the "partition function" f by

$$G(T, P) = -NkT \log f(\beta, P) \qquad (1.10)$$

with $\beta = 1/kT$, (1.7) yields the differential equation

$$-\frac{\partial f}{\partial \beta} = \left(\frac{1}{2\beta} + \frac{P}{b} - \frac{a+P}{\beta}\frac{\partial}{\partial P} - a\sigma\right) f . \qquad (1.11)$$

If we assume

$$f = \text{const.}\ \frac{e^{-\beta P(\sigma + \frac{1}{b})}}{\beta}\left(\frac{a+P}{a}\right)^{\frac{\beta(a+P)}{b} - \frac{1}{2}} \Phi(\beta, P) \qquad (1.12)$$

we see that Φ satisfies the equation

$$\left(\beta \frac{\partial}{\partial \beta} - (a+P)\frac{\partial}{\partial P}\right) \Phi = 0 \tag{1.13}$$

which means that Φ is a function of $\dfrac{\beta(a+P)}{b}$, or

$$\Phi = \Phi\left(\frac{\beta(a+P)}{b}\right) \tag{1.14}$$

where Φ remains as an arbitrary function in the frame-work of themodynamics. We note that (1.9) gives the equation of state

$$L = N\sigma - \frac{N}{b}\log\frac{a+P}{a} + \frac{kT}{2(a+P)} - \frac{N}{b}\frac{\Phi'}{\Phi} . \tag{1.15}$$

The same problem can be treated following the standard method of thermodynamics by introducing entropy S by the second law of thermodynamics,

$$dE = TdS - PdL . \tag{1.16}$$

Then, (1.7) gives

$$\begin{aligned} TdS &= \frac{Nk}{2}dT + \frac{N}{b}dP + (a+P)dL \\ &= \left(\frac{N}{2}k + \frac{N}{b}\frac{\partial P}{\partial T}\right)dT + \left(\frac{N}{b}\frac{\partial P}{\partial L} + a + P\right)dL . \end{aligned} \tag{1.17}$$

The requirement that S(T,L) is a tatal differential, that is

$$\frac{\partial}{\partial T}\frac{\partial S}{\partial L} = \frac{\partial}{\partial L}\frac{\partial S}{\partial T} , \tag{1.18}$$

leads to

$$\left(-\frac{N}{b}\frac{\partial}{\partial L} + T\frac{\partial}{\partial T}\right)\frac{a+P}{T} = 0 . \tag{1.19}$$

Integrating we can write the result as

$$L = N\sigma - \frac{N}{b}\log\frac{bkT}{a} - \frac{N}{b}\psi\left(\frac{a+P}{bkT}\right) \tag{1.20}$$

where the function ψ remains arbitrary in the frame-work of thermodynamics. However, comparing (1.15) with (1.19) we obtain the following relation between Φ and ψ :

$$\psi(z) = \log z - \frac{1}{2z} + \frac{\Phi'(z)}{\Phi(z)} \quad . \tag{1.21}$$

§2. Partition Function

The partition function (per particle of the lattice) for a pressure ensemble is given as $(\gamma = \beta P = P/kT)$

$$f(\beta,\gamma) = \iint_{-\infty}^{\infty} \frac{dp\,dr}{h} e^{-\beta H - \gamma r} \tag{2.1}$$

with the Hamiltonian $H = \frac{1}{2m}p^2 + \phi(r)$. We have

$$f(\beta,\gamma) = \left(\frac{2\pi m}{\beta h^2}\right)^{1/2} Q(\beta,\gamma) \tag{2.2}$$

where

$$Q(\beta,\gamma) = \int_{-\infty}^{\infty} dr\; e^{-\beta\phi_P(r)} \tag{2.3}$$

and ϕ_P is the effective potential, which includes the effect of the pressure P, defined by

$$\begin{aligned}\phi_P(r) &= \frac{a}{b}\left(e^{-b(r-\sigma)} - 1\right) + a(r-\sigma) + Pr \\ &= \frac{a+P}{b}\left\{\left(e^{-b(r-\sigma')} - 1\right) + b(r-\sigma')\right\} \\ &\quad + (a+P)(\sigma' - \sigma) + P\left(\sigma + \frac{1}{b}\right)\end{aligned} \tag{2.4}$$

where σ' is the effective diameter defined by

$$\sigma' = \sigma + \frac{1}{b} \log \frac{a}{a+P} \; . \tag{2.5}$$

Writing

$$z = \frac{\beta(a+P)}{b} \; , \tag{2.6}$$

we get

$$Q = \frac{e^{-\beta P(\sigma + \frac{1}{b})}}{b} \left(\frac{a+P}{a}\right)^{\frac{\beta(a+P)}{b}} \sqrt{\frac{2\pi}{z}}\, \Phi(z) \tag{2.7}$$

where we have introduced the function Φ by

$$\sqrt{\frac{2\pi}{z}}\, \Phi(z) = \int_{-\infty}^{\infty} e^{-z(e^{-x}-1+x)} dx \; . \tag{2.8}$$

Comparing (2.2) and (2.7) with (1.12), we see that the function $\Phi(z)$ here is identical to the function we had introduced in the first section.

Since the effect of pressure is simply expressed by the first and the second factors of the right-hand-side of (2.7), and the argument z, it is sufficient to deal with the case of P=0, to study the property of the function $\Phi(z)$.

When P=0, we have

$$Q = \sqrt{\frac{2\pi}{z_0}}\, \Phi(z_0) \; , \qquad z_0 = \beta \frac{a}{b} \tag{2.9}$$

and the partition function reduces to

$$f(\beta) = \frac{1}{\beta \hbar \omega_0} \Phi(z_0) \qquad \left(\omega_0 = \sqrt{\frac{ab}{m}}\right) . \tag{2.10}$$

In the right-hand-side of (2.10), the factor $1/\beta\hbar\omega_0$ is the well-known partition function of a harmonic oscillator, and therefore the second factor $\Phi(z_0)$ represents the effect of unharmonicity.

§ 3. Binet's Formula

To study the integral in (2.8), we write

$$I = \int_{-\infty}^{\infty} e^{-z\phi(x)}\,dx \,. \tag{3.1}$$

(1) In the harmonic case $\phi(x) = \frac{1}{2}x^2$, we have

$$I = \sqrt{\frac{2\pi}{z}} \,. \tag{3.2}$$

(2) For the exponential interaction

$$\phi(x) = e^{-x} - 1 + x = \frac{x^2}{2!} - \frac{x^3}{3!} + \frac{x^4}{4!} - \cdots \tag{3.3}$$

we have the harmonic term $x^2/2$ as well as the unharmonic terms $-x^3/3! + x^4/4! - \cdots$. In this case (2,8) implies that

$$\begin{aligned} I &= \int_{-\infty}^{\infty} e^{-z(e^{-x}-1+x)}dx \\ &= \int_{-\infty}^{\infty} e^{-\frac{z}{2}x^2} \exp\left\{ z\left(\frac{x^3}{3!} - \frac{x^4}{4!} + \cdots\right)\right\} dx \\ &= \sqrt{\frac{2\pi}{z}}\,\Phi(z) \,. \end{aligned} \tag{3.4}$$

The function $\Phi(z)$ thus stands for the effect of the unharmonic terms.

On the other hand, by some change of the variable, we see that

$$I = z^{-z} e^{z}\, \Gamma(z) \tag{3.5}$$

Thus, $\Phi(z)$ is related to the gamma function $\Gamma(z)$, and therefore we have well-known expressions for it.

One of them, given by Binet[1)], is

$$\log \Phi(z) = 2\int_0^{\infty} \frac{\arctan t/z}{e^{2\pi t} - 1}\,dt \,. \tag{3.6}$$

By partial integration we may write

$$\log \Phi(z) = \frac{1}{\pi} \int_0^\infty \frac{dt}{1+t^2} \log \left(1 - e^{-2\pi z t}\right)^{-1}, \qquad (3.7)$$

or

$$\log \Phi(z) = \frac{1}{\pi} \int_0^{\pi/2} \log \left(1 - e^{-2\pi z \tan \zeta}\right)^{-1} d\zeta \, . \qquad (3.8)$$

Since $z = a/bkT$ when P=0, the last expression looks as if the unharmonicity would give rise to nonlinear modes, not those of solitons but certain excitation, with the energy unit $\frac{a}{b} 2\pi \tan \zeta$.

§ 4. Nonlinear Waves at Finite Temperatures

Now we turn to the problem of the nonlinear wave propagation in the lattice al finite temperatures. Many solitons are being excited and the wave under consideration propagates through the lattice interacting with these solitons.

For comparison we first consider the case of the well-known linear sound wave in a gas. Then we have the wave equation

$$c_0^{-2} \frac{\partial^2 u}{\partial t^2} = \frac{\partial^2 u}{\partial x^2} \qquad (4.1)$$

with

$$c_0^2 = \frac{dP}{d\rho} = \gamma \frac{RT}{M} \qquad (4.2)$$

where ρ is the density, $\gamma = c_p/c_v$ the specific heat ratio, R the so-called gas constant, and M the molecular weight. We note that the velocity c_0 is temperature dependent, reflecting the fact that there are already thermal excitations in the medium.

In the nonlinear case, we may write ($\bar{r}_0 = \bar{r}(P=0)$)

$$P = -\kappa \left((\bar{r} - \bar{r}_0) + \alpha (\bar{r} - \bar{r}_0)^2 \right) , \qquad (4.3a)$$

$$L = N\bar{r} , \tag{4.3b}$$

$$\rho = \frac{Nm}{L} , \tag{4.3c}$$

and
$$\frac{dP}{dL} = \frac{1}{N}\frac{dP}{d\bar{r}} = -\frac{\kappa}{N}\left(1+2\alpha(\bar{r}-\bar{r}_0)\right), \tag{4.4a}$$

$$\frac{d^2P}{dL^2} = -\frac{2\alpha\kappa}{N^2} . \tag{4.4b}$$

In such a case, we have the nonlinear wave equation due to Boussinesq and to Zabusky,

$$c_0^{-2}\frac{\partial^2 y}{\partial t^2} = \left(1+\varepsilon\frac{\partial y}{\partial x}\right)\frac{\partial^2 y}{\partial x^2} + \frac{\bar{r}^2}{12}\frac{\partial^4 y}{\partial x^4} \tag{4.5a}$$

with

$$c_0 = \bar{r}\sqrt{\kappa/m} , \quad \varepsilon = 2\alpha\bar{r} . \tag{4.5b}$$

Remembering (1.20), we get (when P=0)

$$\frac{dP}{dL} = -\frac{b^2kT}{N\psi'(z)} = -\frac{\kappa}{N} \tag{4.6a}$$

$$\frac{d^2P}{dL^2} = \frac{b^2kT\psi''(z)}{N[\psi'(z)]^2}\frac{1}{bkT}\frac{dP}{dL}$$

$$= -\frac{b\psi''(z)\kappa}{N^2[\psi'(z)]^2} = -\frac{2\alpha\kappa}{N^2} . \tag{4.6b}$$

So that

$$\kappa = \frac{b^2kT}{\psi'(z)} \tag{4.7}$$

$$2\alpha = \frac{b\psi''(z)}{[\psi'(z)]^2} \tag{4.8}$$

and

$$c_0^2 = \frac{dP}{d\rho} = -\frac{L}{\rho}\frac{dP}{dL} = \left(\frac{L}{N}\right)^2\frac{\kappa}{m} = \left(\frac{L}{N}\right)^2\frac{b^2kT}{m\psi'(z)}, \tag{4.9}$$

$$\varepsilon = 2\alpha \frac{L}{N} = \frac{L}{N} \frac{b\psi''(z)}{[\psi'(z)]^2} . \tag{4.10}$$

These values of c_0 and ε , together with (4.5), furnish the nonlinear wave equation at finite temperatures.

To chech our results, we examine the case P=0, and $T \to 0$. In this case we have $z = z_0 = a/bkT$ and $z_0 \gg 1$, so that

$$\psi(z) = \log z - \frac{1}{2z} + O\left(\frac{1}{z^2}\right) , \tag{4.11a}$$

$$\psi'(z) = \frac{1}{z} + O\left(\frac{1}{z^2}\right) , \tag{4.11b}$$

$$\psi''(z) = -\frac{1}{z^2} + O\left(\frac{1}{z^3}\right) . \tag{4.11c}$$

Therefore in the limit of low temperatute, we have

$$c_0 \simeq \frac{L}{N}\sqrt{\frac{ab}{m}} = \bar{r}\sqrt{\frac{\kappa}{m}} \qquad (\kappa = ab) \tag{4.12a}$$

$$\varepsilon \simeq -\frac{L}{N} b = 2\alpha_0 \bar{r} \qquad (\alpha_0 = -b/2) \tag{4.12b}$$

which coincide with the well-known values.

Reference

1) see E.T. Whittaker and G.N. Watson, "A Course of Modern Analysis" (Cambridge University Press,1927) p.250