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CONVEX PROPERTIES OF THE GRAND CANONICAL POTENTIAL

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With the technic of the functional derivative it is shown that the thermodynamic potential $\Omega(T, V, \mu)$ possesses certain convex properties. This fact is applied to Wentzel's method of the thermodynamic equivalent Hamiltonian [1] to obtain inequalities which can easily be calculated.

I. INTRODUCTION

In statistical mechanics the computation of lower and upper bounds for physical expressions plays a considerable role. In this article such bounds are calculated for the grand canonical thermodynamic potential $\Omega = \Omega(T, V, \mu)$ of a system of fermions or bosons enclosed in a volume V at temperature T. μ is the chemical potential. The estimates are deducted from general convex properties of the potential Ω. Certain variable parameters are introduced. By such means one gains a variability which in some cases can be exploited to obtain simple results. This is illustrated by the context with G. Wentzel's [1] method of the "thermodynamic equivalent Hamiltonian" (*TEH*). The *TEH*-method plays a role in statistical physics because it allows within the thermodynamic limit ($N \to \infty$, $V \to \infty$, $N/V =$ *constant*) an exact solution of an appropriate given problem.

II. CONVEX PROPERTIES OF THE POTENTIAL

We consider a system of fermions or bosons which is described by a Hamiltonian of the form

$$H(X) = \int d1 \psi^+(1)\{H_0(1) + X(1)\}\psi(1) + \tfrac{1}{2} \int d1 d2 \psi^+(1)\psi^+(2) V(1, 2)\psi(2)\psi(1) \tag{1}$$

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$$F(X) = F(\sum a_\nu \Phi_\nu) = F(a_1, a_2, \ldots, a_M) = F(\mathfrak{a}),$$

$$\mathfrak{a} = (a_1, a_2, \ldots, a_M).$$

Applying the relations (5), (6), (11) and the orthonormality of the Φ_ν, we find

$$\int \mathrm{d}1\mathrm{d}2\Phi_\alpha(1)G(1, 2; X)\Phi_\beta(2) = \frac{\partial^2 F(\mathfrak{a})}{\partial a_\alpha \partial a_\beta}. \qquad (12)$$

Further we define the (M, M)-matrix

$$\mathfrak{B} = \mathfrak{B}(\mathfrak{a}) = \left(\frac{\partial^2 F(\mathfrak{a})}{\partial a_\alpha \partial a_\beta}\right); \ \alpha, \beta = 1, 2, \ldots, M;$$

take $\mathfrak{a}$ as a real M-dimensional column vector, $\mathfrak{a}'$ as the transposed vector and evaluate the quadratic form $\mathfrak{a}'\mathfrak{B}\mathfrak{a}$. With the help of (8), (9) and (12) we arrive at

$$\mathfrak{a}'\mathfrak{B}\mathfrak{a} = \sum_{\alpha,\beta} a_\alpha \frac{\partial^2 F(\mathfrak{a})}{\partial a_\alpha \partial a_\beta} a_\beta = \sum_{\alpha,\beta} a_\alpha a_\beta \int \mathrm{d}1\mathrm{d}2\Phi_\alpha(1)G(1, 2; X)\Phi_\beta(2) =$$

$$= \sum_{\alpha,\beta} a_\alpha a_\beta \int \mathrm{d}1\Phi_\alpha(1)\lambda_\beta\Phi_\beta(1) = \sum_\alpha a_\alpha^2\lambda_\alpha \geq 0.$$

We see that the matrix $\mathfrak{B}$ is positiv semidefinite. Therefore it follows that $F(\mathfrak{a})$ is convex in the real M-dimensional space R_M [6]. This means $F(X) = F(\mathfrak{a})$ satisfies

$$F(\eta\mathfrak{a}_1 + (1-\eta)\mathfrak{a}_2 \leq \eta F(\mathfrak{a}_1) + (1-\eta)F(\mathfrak{a}_2); \quad 0 \leq \eta \leq 1, \qquad (13)$$

$$F(\mathfrak{a}_1) - F(\mathfrak{a}_2) \geq \sum_\alpha (a_\alpha^{(1)} - a_\alpha^{(2)}) \frac{\partial F(\mathfrak{a}_2)}{\partial a_\alpha^{(2)}} \equiv (\mathfrak{a}_1 - \mathfrak{a}_2)' \operatorname{grad}_{\mathfrak{a}_2} F(\mathfrak{a}_2). \qquad (14)$$

Applying (13) twice and looking at the definition (4), we find for the thermodynamic potential the inequality $(\eta \neq 0)$

$$\eta\Omega\left(\left(1-\frac{1}{\eta}\right)\mathfrak{a}\right) + (1-\eta)\Omega(\mathfrak{a}) \leq \Omega(0) \leq \frac{1}{\eta}\Omega((1-\eta)\mathfrak{a}) + \left(1-\frac{1}{\eta}\right)\Omega(\mathfrak{a}), \qquad (15)$$

$\Omega(0) = \Omega$ is the potential we are interested in. The left-hand side of (15) one can estimate further with the help of (4) and (13):

$$\eta^n\Omega\left(\left(1-\frac{1}{\eta^n}\right)\mathfrak{a}\right) + (1-\eta^n)\Omega(\mathfrak{a}) \leq \eta^m\,\Omega\left(\left(1-\frac{1}{\eta^m}\right)\mathfrak{a}\right) + (1-\eta^m)\Omega(\mathfrak{a}), \qquad (16)$$

for $n \geq m$ and $n, m = 1, 2, \ldots$.
The inequality chains (15) and (16) can be used to estimate the thermodynamic

potential $\Omega(0) = \Omega$ in some practical cases. For this purpose the variability of the parameters η and $\mathfrak{a} = (a_1, a_2, \ldots, a_M)$ can be exploited. In the following the relations (15) and (16) are applied to Wentzel's method of the "thermodynamic equivalent Hamiltonian" [1].

III. METHOD OF THE EQUIVALENT HAMILTONIAN

First we rewrite the Hamiltonian (1) with the relations (2) finding

$$H(X) = \int \mathrm{d}1\psi^+(1)\left\{H_0(1) - \frac{V(0)}{2} + X(1)\right\}\psi(1) + \tfrac{1}{2}\int \mathrm{d}1\mathrm{d}2N(1)V(1, 2)N(2). \qquad (17)$$

We introduce the fluctuation operator

$$\Delta N(1) = N(1) - n(1), \qquad (18)$$

where $n(1)$ shall be a certain c-number function which will be specified later. Introducing the identity

$$N(1)N(2) = \Delta N(1)\Delta N(2) + n(2)N(1) + n(1)N(2) - n(1)n(2)$$

into the operator (17) we gain

$$H(X) = H_0(X) + H', \qquad (19a)$$

$$H_0(X) = E_0 + \int \mathrm{d}1\psi^+(1)\left\{H_0(1) - \frac{V(0)}{2} + \int \mathrm{d}2n(2)V(1, 2) + X(1)\right\}\psi(1), \qquad (19b)$$

$$H' = \tfrac{1}{2}\int \mathrm{d}1\mathrm{d}2\Delta N(1)V(1, 2)\Delta N(2), \qquad (19c)$$

$$E_0 = -\tfrac{1}{2}\int \mathrm{d}1\mathrm{d}2n(1)V(1, 2)n(2). \qquad (19d)$$

We have exploited $V(1, 2) = V(1-2)$ and assumed that $V(0)$ is finite. In a system of charged particles $V(r)$ tends to infinity as $r \to 0$; the corresponding contribution is, however, not an interaction energy term, but a selfenergy term and we must drop it [3], [7]. An exact solution of the problem associated with (19) is, of course, out of question. However, this is possible in the thermodynamic limit ($N \to \infty$, $V \to \infty$, N/V = constant) if the number operator $N(1)$ will be replaced by its diagonal part $N(1) \to N_D(1)$

$$N_D(1) = (\psi^+(1)\psi(1))_D = \sum_\alpha |\mathscr{S}_\alpha(1)|^2 C_\alpha^+ C_\alpha. \qquad (20)$$

Because of (19b) we have the field operator $\psi(1)$ expanded in the manner $\psi(1) = \sum_\alpha \mathscr{S}_\alpha(1)C_\alpha$, where the $\mathscr{S}_\alpha$ satisfy

$$\left\{H_0(1) - \frac{V(0)}{2} + \int d2\, n(2)\, V(1,2) + X(1)\right\} \mathscr{S}_\alpha(1) = \varepsilon_\alpha(X)\mathscr{S}_\alpha(1). \tag{21}$$

In (18) and (19) we replace $N(1)$ by $N_D(1)$. Then there resultes the new (model) Hamiltonian

$$H_M(X) = H_0(X) + H'_M. \tag{22a}$$

$$H_0(X) = E_0 + \sum_\alpha \varepsilon_\alpha(X) C^+_\alpha C_\alpha. \tag{22b}$$

M. D. Girardeau [8] has shown within a perturbation calculation that in the thermodynamic limit (in [8] is $X(1) \equiv 0$) H'_M becomes negligible in the sense that

$$\Omega(0) = -\frac{1}{\beta} \ln Tr \exp\left[-\beta(H_M(0) - \mu N)\right], \tag{23}$$

differs from

$$\Omega_0(0) = -\frac{1}{\beta} \ln Tr \exp\left[-\beta(H_0(0) - \mu N)\right], \tag{24}$$

only by a thermodynamically negligible term provided the c-number function $n(1)$ is chosen in the form

$$n(1) = \langle N(1)\rangle_0 = \langle N_D(1)\rangle_0 = \frac{Tr N_D \exp\left[-\beta(H_0(0) - \mu N)\right]}{Tr \exp\left[-\beta(H_0(0) - \mu N)\right]}. \tag{25}$$

Thus the knowledge of (24) is sufficient in this case. According to (22b) we need the $\varepsilon_\alpha(X)$, i. e. the solutions of the Schrödinger equation (21). Even if $X = 0$, the construction of these eigenvalues is in general not possible. Therefore we want to show that we can get simple inequalities using the general convex properties of the thermodynamic potential Ω, or Ω_0, respectively.

IV. EXPLICIT LOWER AND UPPER BOUNDS

We employ (15) with the substitution $\Omega = \Omega_0$, where Ω_0 is given by (24). In (21) the expansion (10) is used. If one chooses M large enough so that with a sufficient accuracy

$$\int d2\, n(2) V(1,2) \approx \sum_{\alpha=1}^{M} b_\alpha \Phi_\alpha,$$

then one can set (ξ a real parameter)

$$a_\alpha = -\xi b_\alpha \quad \text{or} \quad \mathfrak{a} = -\xi \mathfrak{b}$$

and gets instead of (21)

$$\left\{H_0(1) - \frac{V(0)}{2} + (1-\xi)\int d2\, n(2) V(1,2)\right\} \mathscr{S}_\alpha(1;\xi) = \varepsilon_\alpha(\xi)\mathscr{S}_\alpha(1;\xi). \tag{26}$$

The corresponding thermodynamic potential is in the ξ-notation

$$\Omega_0(\mathfrak{a}) = \Omega_0(-\xi\mathfrak{b}) \equiv \Omega_0(\xi) = -\frac{1}{\beta} \ln Tr \exp\left[-\beta(H_0(\xi) - \mu N)\right],$$

or according to (22b) explicit

$$\Omega_0(\xi) = E_0 - \frac{1}{\beta} \ln Tr \exp\left[-\beta \sum_\alpha (\varepsilon_\alpha(\xi) - \mu) C^+_\alpha C_\alpha\right]. \tag{27}$$

We have also with $0 < \eta \leq 1$

$$\eta\Omega_0\left(1 - \frac{1}{\eta}\right) + (1-\eta)\Omega_0(1) \leq \Omega_0 \leq \frac{1}{\eta}\Omega_0(1-\eta) + \left(1 - \frac{1}{\eta}\right)\Omega_0(1). \tag{28}$$

To calculate $\Omega_0(1)$ we must solve (26), setting $\xi = 1$. In a homogeneous medium, for instance, (with $U(1) \equiv 0$ in (3)) this problem is trivial. To find $\Omega_0(1-\eta)$ we substitute in (26) $\xi = 1 - \eta$ and use the fact that η can be chosen arbitrarily small (but $\eta \neq 0$, of course). Then the standard perturbation theory [2] can be used to find $\varepsilon_\alpha(1-\eta)$. η is the expansion parameter in the perturbation series. With these remarks the upper bound in (28) is considered to be known. Next it is shown that the lower bound in (28) can be estimated to give a very simple result. For this we take (16) with $m = 1$. Thus we have

$$\eta^n\Omega_0\left(1 - \frac{1}{\eta^n}\right) + (1-\eta^n)\Omega_0(1) \leq \eta\Omega_0\left(1 - \frac{1}{\eta}\right) + (1-\eta)\Omega_0(1) \leq \Omega_0. \tag{29}$$

Further the general inequalities [9]

$$Tr \exp(A+B) \leq Tr \exp A \exp B \leq (Tr \exp 2A)^{1/2} (Tr \exp 2B)^{1/2}, \tag{30}$$

are valid for the Hermitean operators A and B. (The existence of the Tr-operation is assumed). We write

$$H_0(\xi) - \mu N = \int d1\, \psi^+(1)\left\{H_0(1) - \mu - \frac{V(0)}{2} + (1-\xi)\int d2\, n(2) V(1,2)\right\}\psi(1) =$$

$$= H'_0 - \xi W,$$

$$W = \int d1\, d2\, n(2) V(1,2) N(1) = \sum_{\alpha,\beta} W_{\alpha\beta} C^+_\alpha C_\beta \tag{31}$$

and define

$$A = -\beta H_0'; \quad B = \beta \xi_n W; \quad \xi_n = 1 - \eta^{-n}; \quad 0 < \eta < 1.$$

Introducing these definitions into (30) we have gained

$$\Omega_0(\xi_n) = -\frac{1}{\beta} \ln Tr \exp[-\beta(H_0' - \xi_n W)] \geq -\frac{\beta}{2} [\ln Tr \exp(-2\beta H_0') + \\ + \ln Tr \exp(2\beta \xi_n W)]$$

and we can estimate (29) in the manner

$$-\frac{\beta}{2} \eta^n \ln Tr \exp(-2\beta H_0') - \frac{\beta}{2} \eta^n \ln Tr \exp(2\beta \xi_n W) + \\ + (1 - \eta^n)\Omega_0(1) \leq \eta^n \Omega_0(\xi_n) + (1 - \eta^n)\Omega_0(1) \leq \Omega_0. \qquad (32)$$

Since $\ln Tr \exp(-2\beta H_0')$ is independent of n and $0 < \eta < 1$ the first term on the left-hand side of (32) can be made arbitrarily small if n is sufficient high. The second term on the lefthand side of (32) is calculated explicitly in the abstract occupationnumber Hilbert space. Looking at (31), we find

$$Tr \exp(2\beta \xi_n W) = \sum_{n_1, \ldots, n_\infty} \langle n_1, \ldots, n_\infty | \exp(2\beta \xi_n \sum_{\alpha, \beta} W_{\alpha\beta} C_\alpha^+ C_\beta) | n_1 \ldots, n_\infty \rangle =$$

$$= \sum_{n_1, \ldots, n_\infty} \langle n_1, \ldots, n_\infty | \exp(2\beta \xi_n \sum_\alpha W_{\alpha\alpha} C_\alpha^+ C_\alpha | n_1 \ldots n_\infty \rangle =$$

$$= \prod_\alpha Tr \exp(2\beta \xi_n W_{\alpha\alpha} C_\alpha^+ C_\alpha) = \prod_\alpha (1 \pm \exp(2\beta \xi_n W_{\alpha\alpha}))^{\pm 1} -$$

$$-\frac{\beta}{2} \eta^n \ln Tr \exp(2\beta \xi_n W) = \mp \frac{\beta}{2} \eta^n \sum_\alpha \ln[1 \pm \exp(2\beta \xi_n W_{\alpha\alpha})],$$

(upper sign: fermions; lower sign: bosons). It is reasonable to assume $W_{\alpha\alpha} > 0$. Then we arrive at

$$\lim_{n \to \infty} \eta^n \sum_\alpha \ln[1 \pm \exp(2\beta \xi_n W_{\alpha\alpha})] = 0; \quad 0 < \eta < 1.$$

Therefore the inequality (32) leads to the simple result

$$\Omega_0(1) \leq \Omega_0,$$

giving the final lower and upper bounds

$$\Omega_0(1) \leq \Omega_0 \leq \frac{1}{\eta} \Omega_0(1 - \eta) + \left(1 - \frac{1}{\eta}\right) \Omega_0(1); \quad 0 < \eta < 1. \qquad (33)$$

V. DISCUSSION

We have derived fairly general convex properties of the grand canonical potential in a domain of the real M-dimensional number space R_M. This enabled us to write the inequality chains (15) and (16) for the thermodynamic potential Ω. The estimates (15) and (16) are valuable if one can choose the parameters a and η in such a manner that the corresponding thermodynamic potentials can be calculated. This is the case, for example, in the theory of the thermodynamic equivalent Hamiltonian. We have shown that in this framework the grand canonical potential possesses lower and upper bounds (see inequality (33)), which can easily be calculated. What one must do is to choose suitably a number of parameters.

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