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## Inequalities for liquids in a periodic potential

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**Abstract.** For any two unitarily related Hamiltonians  $H$  and  $H'$  we point out the existence of the inequality  $\langle H' - H \rangle_H \geq 0$  and present applications to the density distribution of interacting mobile particles embedded in a periodic medium. Other applications (to e.g. spin systems) are also discussed.

### 1. Inequalities

For any two Hamiltonians  $H$  and  $H'$  we have the inequality (see e.g. Feynman 1972)

$$F' + \langle H' - H \rangle_H \geq F \quad (1)$$

where the free energies  $F$  and  $F'$  are defined respectively by  $\exp(-\beta F) \equiv \text{Tr} \exp(-\beta H)$  and  $\exp(-\beta F') \equiv \text{Tr} \exp(-\beta H')$  and  $\beta \equiv 1/k_B T$  is the inverse temperature. The thermal average for an arbitrary operator  $B$  is given by

$$\langle B \rangle_H \equiv \text{Tr} B \exp[\beta(F - H)]. \quad (2)$$

In particular, when  $H$  and  $H'$  are unitarily related, i.e.

$$H' = e^{iA} H e^{-iA} \quad (3)$$

with  $A = A^\dagger$  being Hermitian, the two operators  $H$  and  $H'$  have identical energy spectrum and hence  $F = F'$ . Then equation (1) implies

$$\langle H' - H \rangle_H \geq 0. \quad (4)$$

This inequality can be applied straightforwardly to several systems. For example, for interacting mobile particles embedded in a periodic medium the Hamiltonian is given by

$$H = H_0 + \int dx \hat{\rho}(x) V(x) \quad (5)$$

where  $H_0$  is that part of the Hamiltonian which is invariant under spatial translations and rotations.  $\hat{\rho}(x)$  and  $V(x)$  are the density operators and the single particle potential simulating the periodic medium, respectively. For inequality (1) and therefore (4) to be applicable, it is necessary to impose periodic boundary conditions on the wavefunctions, which in this way become square integrable functions.

## 2. Density of inhomogeneous liquid

The Hamiltonian (5) applies to several systems of recent interest, e.g. superionic conductors (Dieterich *et al* 1981), intercalation system (Bunde and Dieterich 1981a) and submonolayer films on periodic substrates (Nielsen *et al* 1978). In a superionic conductor, for example,  $H_0$  describes the interaction between the mobile ions. The cage ions are located at regular lattice sites and represent the periodic medium, which gives rise to the periodic potential. A further example is a non-uniform interacting electron system.

Due to the different characteristic lengths involved in equation (5), e.g. interaction length and period of  $V(\mathbf{x})$ , equation (5) has been used to study commensurability effects (Guyer and Miller 1979). In general, the static and dynamic properties of equation (5) cannot be obtained exactly and rigorous results, even for the density distribution  $\rho(\mathbf{x})$ , are absent. For an exception, see Guyer and Miller (1979). Meaningful approximations, e.g. inhomogeneous Percus–Yevick equations coupled to the Yvon–Born–Green hierarchy (see Bunde and Dieterich 1981b), can only be treated with a considerable amount of numerical work.

In contrast, simple rigorous results for the density distribution of the complicated system can be obtained easily from equations (4) and (3), as we will show immediately. Putting  $A = \mathbf{b} \cdot \mathbf{P}$  in equation (3) where  $\mathbf{b}$  is an arbitrary displacement and  $\mathbf{P}$  is the momentum operator we obtain from equations (4) and (5) after dividing by the volume  $V_0$  and taking the limit  $V_0 \rightarrow \infty$

$$f(\mathbf{b}) \equiv \frac{1}{\Omega} \int_{\Omega} d\mathbf{x} [\rho(\mathbf{x} - \mathbf{b}) - \rho(\mathbf{x})] V(\mathbf{x}) \geq 0 \quad (6)$$

where  $\Omega$  denotes the elementary cell defined by the periodicity of the single particle potential. In deriving equation (6) we have used  $[H_0, \mathbf{P}] = 0$  and  $\exp(i\mathbf{b} \cdot \mathbf{P}) \hat{\rho}(\mathbf{x}) \exp(-i\mathbf{b} \cdot \mathbf{P}) = \hat{\rho}(\mathbf{x} - \mathbf{b})$ . We note that the inequality (6) holds for all temperatures, interactions, concentrations of the mobile particles and displacements  $\mathbf{b}$ . It generalises an inequality which has been derived earlier by Theophilou (private communication) for the inhomogeneous electron system at zero temperature.

It is convenient to introduce the Fourier expansions

$$V(\mathbf{x}) = \sum_{\mathbf{G}} V_{\mathbf{G}} \exp(i\mathbf{G} \cdot \mathbf{x}) \quad (7)$$

and

$$\rho(\mathbf{x}) = \sum_{\mathbf{G}} \rho_{\mathbf{G}} \exp(i\mathbf{G} \cdot \mathbf{x}) \quad (8)$$

where  $\mathbf{G}$  denotes the reciprocal lattice vectors associated with the periodicity of  $V(\mathbf{x})$ . Since  $V(\mathbf{x})$  and  $\rho(\mathbf{x})$  are real,  $V_{\mathbf{G}}$  and  $\rho_{\mathbf{G}}$  must satisfy the relations  $V_{-\mathbf{G}} = V_{\mathbf{G}}^*$  and  $\rho_{-\mathbf{G}} = \rho_{\mathbf{G}}^*$ . Inserting equations (7) and (8) into equation (6) we obtain

$$\sum_{\mathbf{G}} \rho_{\mathbf{G}} V_{\mathbf{G}}^* [1 - \exp(-i\mathbf{G} \cdot \mathbf{b})] \leq 0. \quad (9)$$

When  $V(\mathbf{x})$  satisfies inversion symmetry, equation (9) yields

$$\sum_{\mathbf{G}} \rho_{\mathbf{G}} V_{\mathbf{G}} \sin^2(\frac{1}{2}\mathbf{G} \cdot \mathbf{b}) \leq 0. \quad (10)$$

Now we take  $\mathbf{b} = \alpha \mathbf{a}_{i,0}$  where  $\alpha$  is an arbitrary constant,  $\mathbf{a}_{i,0}$  is one of the three lattice vectors and write  $\mathbf{G}$  in terms of the basic reciprocal lattice vectors  $\mathbf{G}_{i,0}$ . Using the

reciprocity relation  $\mathbf{G}_{i,0} \cdot \mathbf{a}_{j,0} = 2\pi\delta_{ij}$  we obtain from equation (10) for  $\alpha = \frac{1}{2}$

$$\sum_{n=0}^{\infty} \rho_{(2n+1)\mathbf{G}_{i,0}} V_{(2n+1)\mathbf{G}_{i,0}} \leq 0, \quad i = 1, 2, 3 \tag{11}$$

while in the limit  $\alpha \rightarrow 0$  we find

$$\sum_{n=1}^{\infty} n^2 \rho_{n\mathbf{G}_{i,0}} V_{n\mathbf{G}_{i,0}} \leq 0, \quad i = 1, 2, 3. \tag{12}$$

In deriving equation (12) we have assumed that  $V(\mathbf{x})$  can be expressed by a finite number of Fourier coefficients  $V_{\mathbf{G}}$ . The relations (9)–(12) represent general non-trivial inequalities for the density distribution.

### 3. Specific examples

To be specific, let us consider the case of a classical liquid which is embedded in a periodic potential. The total energy is written as

$$V_{\text{tot}}(\mathbf{r}_1, \dots, \mathbf{r}_N) = \sum_{k,1} V^{(2)}(\mathbf{r}_k - \mathbf{r}_1) + \sum_k V(\mathbf{r}_k) \tag{13}$$

where  $\mathbf{r}_k$  denotes the instantaneous position of the  $k$ th particle.  $V^{(2)}$  is the pair potential between two particles and  $V$  is the external potential. Our bounds (11) and (12) do not depend explicitly on the form of  $V^{(2)}$ , but depend strongly on the shape of the external potential. For example, for a simple one-dimensional sinusoidal potential where  $V(x) = \frac{1}{2}V_1 \cos(G_{1,0}x)$  we have  $V_{\mathbf{G}} = V_{-\mathbf{G}} = V_1 \delta_{\mathbf{G},G_{1,0}}$  and we obtain from equation (11)

$$\rho_{G_{1,0}} V_{G_{1,0}} \leq 0. \tag{14}$$

Thus the density fluctuation Fourier coefficient has the opposite sign to the corresponding Fourier coefficient of the external potential.

For a one-dimensional potential with two non-equivalent minima described by

$$V(x) = \frac{1}{2}V_1 \cos(G_{1,0}x) + \frac{1}{2}V_2 \cos(2G_{1,0}x) \tag{15}$$

we have  $V_{\mathbf{G}} = V_{-\mathbf{G}} = V_1 \delta_{\mathbf{G},G_{1,0}} + V_2 \delta_{\mathbf{G},2G_{1,0}}$ . Then we find from equations (11) and (12)

$$\rho_{G_{1,0}} V_{G_{1,0}} \leq 0 \tag{16}$$

$$\rho_{2G_{1,0}} V_{2G_{1,0}} \leq \frac{1}{4} |\rho_{G_{1,0}} V_{G_{1,0}}|. \tag{17}$$

Generalisations to more complicated potentials are straightforward.

For non-interacting particles  $\rho(\mathbf{x})$  can be calculated exactly by three-dimensional numerical integration. Including the interaction, however,  $\rho(\mathbf{x})$  has only been calculated exactly for the particular case of harmonically bound particles in a sinusoidal potential (Frenkel–Kontorova model), and even for this case a large amount of numerical work is needed. In general,  $\rho(\mathbf{x})$  cannot be calculated rigorously and analytical solutions do not exist. Therefore our bounds offer a simple non-trivial check of the approximation scheme used to calculate  $\rho(\mathbf{x})$ . In addition, since many numerical procedures involve iteration schemes, the inequalities may be used to check the convergency of the different iteration schemes.

#### 4. Discussion

Note that the Hermitian operator  $A$  in equation (3) is arbitrary. By choosing a new  $A$  we get new inequalities from equation (4). For example, when  $A = \mathbf{b} \cdot \mathbf{L}$  with  $\mathbf{L}$  being the angular momentum operator, we have from equations (3) to (5)

$$\int d\mathbf{x} \rho(\mathbf{x}) [V(\mathbf{x} + \mathbf{b} \times \mathbf{x}) - V(\mathbf{x})] \geq 0. \quad (18)$$

We now consider the spin Hamiltonian

$$H = D \sum_i (S_i^z)^2 + E \sum_i [(S_i^x)^2 - (S_i^y)^2] - \sum_{ij} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j \quad (19)$$

which has been used (Cisneros Ramos and Sivardiere 1976) in describing ferromagnets  $\text{HoFeO}_3$ ,  $\text{TmCrO}_3$ , etc. Under a rotation of  $\pi/2$  around the  $z$  axis,  $[(S_i^x)^2 - (S_i^y)^2]$  changes sign while the remaining terms in equation (19) are unchanged. Therefore,

$$\langle H' - H \rangle = -2E \sum_i \langle (S_i^x)^2 - (S_i^y)^2 \rangle \geq 0. \quad (20)$$

When  $S = 1$ , the second term in equation (19) may be interpreted as the flipping between the doublets in the three-level system. Equation (20) then says that this flipping always lowers the energy of the system and makes it more stable.

It should be emphasised that the only two conditions for equation (4) to hold are: (i) Both  $H$  and  $H'$  are Hermitian; (ii)  $H$  and  $H'$  have identical spectrum. Unitary transformations (and maybe other more general relations) between Hamiltonians  $H$  and  $H'$  are special cases that fulfil these two conditions. Since equation (1) is valid for both quantum and classical systems (see e.g. Falk 1970) so must equation (4) be. Also, we note that equation (4) is valid for an arbitrary system, whether it is one-particle or many-particle, fermions or bosons.

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#### References

- Bunde A and Dieterich W 1981a *Physics of intercalation compounds* ed L Pietronero and E Tosatti (Berlin: Springer)  
 — 1981b *Solid State Commun.* **37** 229  
 Cisneros Ramos L and Sivardiere J 1976 *Solid State Commun.* **19** 907  
 Dieterich W, Fulde P and Peschel I 1981 *Adv. Phys.* **29** 527  
 Falk H 1970 *Am. J. Phys.* **38** 858  
 Feynman R P 1972 *Statistical Mechanics* (Reading, Mass.: Benjamin) p 67  
 Guyer R A and Miller M D 1979 *Phys. Rev. Lett.* **42** 718  
 Nielsen M, McTague J P and Ellenson W 1977 *J. Physique C* **38** 4