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On a unified treatment of molecular interactions at finite temperatures*

S. Baer and A. Ben-Shaul

The Hebrew University, Department of Physical Chemistry, Jerusalem, Israel

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The by now standard expression for the free energy of interaction of a pair of molecules in terms of molecular susceptibilities at imaginary frequencies follows from a straightforward perturbation expansion of the statistical operator $\exp(-\beta H)$ and from the possibility to express the terms in the expansion in terms of intramolecular charge density correlations at imaginary times.

The method, to be presented here, for studying interactions between molecules is based on the following considerations:

(1) The interaction energy is entirely determined by the electromagnetic interactions between the electric charges in the different molecules. Assuming presently that the interactions are instantaneous, they reduce to the simple Coulomb interactions between the charges.

(2) If the system of molecules is immersed in a heat bath, the most direct quantity for measuring the interactions between them is the Helmholtz free energy of interaction ΔF defined as the difference between the free energy F_0 of the system of noninteracting molecules, and F , the free energy of the system of interacting molecules. The energy of interaction E can be obtained by the Gibbs-Helmholtz relation

$$\Delta E = (\partial/\partial\beta)(\beta\Delta F), \quad (1)$$

where $\beta = 1/(kT)$ is the reciprocal temperature. At absolute zero temperature this reduces to

$$\Delta E = \lim_{\beta \rightarrow \infty} \Delta F. \quad (2)$$

(3) The free energy ΔF can be given in form of a perturbation expansion in terms of the interaction energy operator V related to the Hamiltonians H_0 and H of the system of noninteracting and interacting molecules, respectively, by

$$H = H_0 + V. \quad (3)$$

The perturbation expansion follows essentially from the expansion of the statistical operator $e^{-\beta H}$ in terms of V .

We shall apply the above considerations to the simple system of a pair of molecules. In this case V is the Coulomb interaction energy operator between the charges of the two molecules and can be written in a compact form in terms of charge density operators¹ $\rho_a(\mathbf{x})$ and $\rho_b(\mathbf{y})$ of the two molecules a and b , respectively:

$$V = \int \int [\rho_a(\mathbf{x})\rho_b(\mathbf{y})/|\mathbf{x} - \mathbf{y}|] d^3\mathbf{x} d^3\mathbf{y}. \quad (4)$$

The charge density operator $\rho(\mathbf{x})$ of a molecule is defined here by its coordinates representation

$$\rho(\mathbf{x}) = \sum_i e_i \delta(\mathbf{x} - \mathbf{x}_i), \quad (5)$$

where δ stands for the Dirac delta function, $\mathbf{x}_i$ and e_i are, respectively, the coordinates and charge of the i th particle in the molecule, and the sum goes over all the charged particles inside the molecule.

The free energy of a system is generally defined by

$$F = -\beta^{-1} \log \text{Tr} e^{-\beta H}, \quad (6)$$

where the trace

$$\text{Tr} e^{-\beta H} = \sum_s \langle s | e^{-\beta H} | s \rangle, \quad (7)$$

with the sum extending over a complete orthonormal set of quantum states $|s\rangle$ of the system, is known as the partition function of the system. Consequently, the free energy of interaction of a pair of molecules is

$$\Delta F = -\beta^{-1} \log(\text{Tr} e^{-\beta H} / \text{Tr} e^{-\beta H_0}). \quad (8)$$

The two traces in the numerator and denominator stand for the partition function of the system of a pair of interacting and noninteracting molecules, respectively. However, some clarification of the appropriate definition for these traces is needed: The traces are defined only when the two molecules are placed in a finite volume, since a complete set of states of molecules includes the unbounded states, and the latter contribute to the trace a volume proportional part which goes to infinity with the volume. Equivalently, the molecules in an infinite volume are almost always, i.e., with probability 1, dissociated into ions and electrons. Therefore we shall discard these states from the partition function of the system of molecules by subtracting from the full trace the trace over the asymptotic states, i.e., the states of noninteracting electrons and ions: In conformity with a previous terminology² we shall take only the "connected part" of the trace and denote this by the

subscript c added to the symbol of the trace and to the expectation values in the sum over states in (7):

$$\text{Tr}_c e^{-\beta H} = \sum_s \langle s | e^{-\beta H} | s \rangle_c. \quad (7')$$

An additional problem arises in the evaluation of (7) for a system of a pair of molecules when the symmetry of the electrons with respect to permutations is considered. Without it we could choose for the set of states $|s\rangle$ the pair of quantum states $|n_a, n_b\rangle$ of the isolated (noninteracting) molecules, but by the exclusion principle the summation in (7) must be restricted to a complete orthonormal set of states in the subspace of states which are antisymmetric with respect to electrons exchange. Yet it can be shown³ (see the Appendix) that the restricted trace still can be given by

$$\text{Tr} e^{-\beta H} = (1/N) \sum_{n_a, n_b} \langle n_a, n_b | e^{-\beta H} A | n_a, n_b \rangle, \quad (9)$$

where A is an antisymmetrizing operator permuting the electrons' coordinates between the two molecules and where N is the number of such permutations. If l and m denote, respectively, the number of electrons in molecule a and molecule b we have necessarily

$$N = (l+m)!/l!m!.$$

The set of states $|n_a, n_b\rangle$ in (9) corresponds to a fixed numbering of the electrons, assigning a set of numbered electrons to molecule a and the rest to molecule b . Other assignments of the numbered electrons to a and b do also lead to quantum mechanically identical states, but these will not appear among the above set. They are obtained, however, by linear combinations of states of the original assignment and one can roughly say that if the atoms are sufficiently far apart the bound states of the different assignments are obtained as a superposition of mainly continuum states of the original assignment, i.e., electrons which in one assignment are far from the nuclei of the molecule to which they are assigned but near the nuclei of the second molecule, are near to the nuclei of their assigned molecule in at least some other assignments. Now if we wish to restrict ourselves only to the connected part of the trace, the bound states of the original assignment alone, out of the total number of N different assignments, will contribute to the trace whereas all bound states should be taken into account in the trace. This can be corrected in an approximate way by multiplying the rhs of (9) by the total number of assignments (N), obtaining³

$$\text{Tr}_c e^{-\beta H} = \sum_{n_a, n_b} \langle n_a, n_b | e^{-\beta H} A | n_a, n_b \rangle_c. \quad (9')$$

This equation, without the factor N^{-1} of (9), has the

correct form for large separation between the pair of molecules when exchange is small. Moreover, when it can be practically neglected, A can even be replaced by unity since all other permutations in A add a negligible contribution to the terms in (9'). Formula (9') has been also adopted in the case of finite separation^{2,4} where it has been derived from other considerations. Presently we shall restrict ourselves entirely to large separations where exchange can be neglected.

We shall make now a perturbation expansion of the statistical operator $e^{-\beta H}$ in powers of the interaction V . The well known expansion^{5,6} can be derived most conveniently from the differential equation for the operator

$$U(\tau) = e^{\tau H_0} e^{-\tau H}, \quad (10)$$

namely,

$$U'(\tau) = -V(\tau)U(\tau), \quad (11)$$

where

$$V(\tau) = e^{\tau H_0} V e^{-\tau H_0} \quad (12)$$

is said to be the interaction representation of the operator V at an imaginary time τ . Writing (11) in the integral form

$$U(\beta) = 1 - \int_0^\beta V(\tau)U(\tau) d\tau \quad (13)$$

and solving it by successive iterations we obtain,

$$e^{-\beta H} = e^{-\beta H_0} (1 + I_1 + I_2 + I_3 + \dots), \quad (14)$$

where

$$I_1 = - \int_0^\beta V(\tau) d\tau, \quad (15)$$

$$I_2 = \int \int_{\beta > \tau_1 > \tau_2 > 0} V(\tau_1) V(\tau_2) d\tau_1 d\tau_2, \quad (16)$$

etc. Substituting (14) into (8) and expanding the logarithm we obtain

$$\Delta F = -\beta^{-1} \{ \langle I_1 \rangle + \langle I_2 \rangle - \frac{1}{2} \langle I_1 \rangle^2 + \dots \}, \quad (17)$$

where the brackets are defined as a thermal averaging over the unperturbed system states, i.e., for any operator O we define

$$\langle O \rangle = Q^{-1} \text{Tr} (e^{-\beta H_0} O), \quad (18)$$

where

$$Q = \text{Tr} e^{-\beta H_0}. \quad (19)$$

Since H_0 decomposes into a sum

$$H_0 = H_a + H_b, \quad (20)$$

where H_a , H_b are, respectively, the Hamiltonians of the molecules a and b , one should note that when the operator O splits into a product

$$O = O_a O_b, \quad (21)$$

where O_a , O_b act on the states of the isolated molecules a and b , respectively, we have

$$Q = Q_a Q_b \quad (22)$$

and the average in (18) splits into a product of averages over the isolated molecules' states:

$$\langle O \rangle = \langle O_a \rangle \langle O_b \rangle. \quad (23)$$

Thus, we conclude from (4) and (15), (16), etc. that all the terms in the expansion (17) become functionals of averages over isolated molecules' states.

Examine now each of the terms in (17) separately. The first term is the lowest order term in the expansion. If we substitute (15) for O in (18) we observe that the trace can be transformed as follows:

$$\begin{aligned} \text{Tr}[e^{-\beta H_0} \int_0^\beta V(\tau) d\tau] &= \int_0^\beta d\tau \text{Tr}(e^{-\beta H_0} e^{\tau H_0} V e^{-\tau H_0}) \\ &= \int_0^\beta d\tau \text{Tr}(e^{-\beta H_0} V). \end{aligned} \quad (24)$$

In the first equality we have put the trace under the integral sign. In the second equality we have used the fact that the trace is invariant to a cyclic permutation of its factors. If the last factor $e^{-\tau H_0}$ is shifted to the beginning of the trace and commuted with $e^{-\beta H_0}$ one sees that it is canceled out by the $e^{\tau H_0}$ factor. Thus we obtain

$$\langle I_1 \rangle = -\beta \text{Tr}(e^{-\beta H_0} V) / \text{Tr} e^{-\beta H_0} = -\beta \langle V \rangle \quad (25)$$

and hence the first order contribution to ΔF is

$$\Delta F_1 = \langle V \rangle, \quad (26)$$

i. e., is equal to the average electrostatic interaction energy between the charges in the two molecules. Substituting from (4) into (26) and noting (21) and (23), we obtain $\langle V \rangle$ in terms of the average charge densities of the isolated molecules:

$$\langle V \rangle = \int \int [\rho_a(\mathbf{x}) \rho_b(\mathbf{y}) / |\mathbf{x} - \mathbf{y}|] d^3\mathbf{x} d^3\mathbf{y}. \quad (27)$$

To evaluate the second term in (17) we substitute now (4), noting (12), into (16) and then into (18). We again utilize the decomposition property (21) and (23) to rewrite $\langle I_2 \rangle$ in terms of intramolecular "pair correlation" functions defined by averages over single molecule states. Thus if we define^{2,6(b)}

$$f_a(x_1, \tau_1, x_2, \tau_2) = \langle T\{\rho_a(x_1, \tau_1) \rho_a(x_2, \tau_2)\} \rangle, \quad (28)$$

where

$$\rho_a(x, \tau) = e^{\tau H_a} \rho_a(x) e^{-\tau H_a} \quad (29)$$

and T denotes an ordering operator of the τ 's dependent factors on its rhs according to decreasing values of the τ 's, we obtain

$$\begin{aligned} \langle I_2 \rangle &= \frac{1}{2} \int_0^\beta \int_0^\beta d\tau_1 d\tau_2 \int \cdots \int [f_a(\mathbf{x}_1, \tau_1, \mathbf{x}_2, \tau_2) f_b \\ &\quad \times (\mathbf{y}_1, \tau_1, \mathbf{y}_2, \tau_2) / |\mathbf{x}_1 - \mathbf{y}_1| |\mathbf{x}_2 - \mathbf{y}_2|] \\ &\quad \times d^3\mathbf{x}_1 d^3\mathbf{x}_2 d^3\mathbf{y}_1 d^3\mathbf{y}_2. \end{aligned} \quad (30)$$

By a slight modification of the definition (28) of the correlation function we can obtain the full second order contribution to the free energy, including the third term in (17). Indeed if we replace the charge density operators in (28) by the excess charge density operators

$$\bar{\rho}(\mathbf{x}, \tau) = \rho(\mathbf{x}, \tau) - \langle \rho(\mathbf{x}) \rangle \quad (31)$$

we get modified correlation functions which we shall distinguish from those defined in (28) by a bar over the function symbol. Substituting the modified functions into (30) we obtain in addition to $\langle I_2 \rangle$, observing (25) and (27), the term

$$- \int_0^\beta \int_0^\beta \langle V \rangle^2 d\tau_1 d\tau_2 = - \langle I_1 \rangle^2. \quad (32)$$

Since the trace implied in (28) is invariant to a cyclic shifting of its factors, the correlation functions defined in (28) and subsequently, depend on τ_1 and τ_2 only through the difference $\tau = \tau_1 - \tau_2$, i. e.,

$$\begin{aligned} \bar{f}_a(\mathbf{x}_1, \tau_1, \mathbf{x}_2, \tau_2) &= \langle T\{\bar{\rho}_a(\mathbf{x}_1, \tau_1 - \tau_2) \bar{\rho}_a(\mathbf{x}_2, 0)\} \rangle \\ &\equiv \bar{f}_a(\mathbf{x}_1, \mathbf{x}_2, \tau). \end{aligned} \quad (33)$$

We can check now that this function, defined in the interval

$$-\beta \leq \tau \leq \beta \quad (34)$$

is a periodic function with a period β and one can make a Fourier expansion

$$\bar{f}(\mathbf{x}_1, \mathbf{x}_2, \tau) = \beta^{-1} \sum_{n=-\infty}^{\infty} \chi_n(\mathbf{x}_1, \mathbf{x}_2) e^{-i\omega_n \tau}, \quad (35)$$

where

$$\omega_n = 2\pi n / \beta, \quad n = 0, \pm 1, \pm 2, \dots \quad (36)$$

and

$$\chi_n(\mathbf{x}_1, \mathbf{x}_2) = \int_0^\beta \bar{f}(\mathbf{x}_1, \mathbf{x}_2, \tau) e^{i\omega_n \tau} d\tau. \quad (37)$$

Furthermore, substituting the expansion (35) corresponding to $\bar{f}_a(\mathbf{x}_1, \mathbf{x}_2, \tau)$ and $\bar{f}_b(\mathbf{x}_1, \mathbf{x}_2, \tau)$ into (30) we can carry out a formal integration of the variables and obtain for the second order free energy of interaction

$$\begin{aligned} -\beta \Delta F_2 &= \frac{1}{2} \sum_{n=-\infty}^{\infty} \int \cdots \int [\chi_{an}(\mathbf{x}_1, \mathbf{x}_2) \chi_{bn}(\mathbf{y}_2, \mathbf{y}_1) / |\mathbf{x}_1 \\ &\quad - \mathbf{y}_1| |\mathbf{x}_2 - \mathbf{y}_2|] d^3\mathbf{x}_1 d^3\mathbf{x}_2 d^3\mathbf{y}_1 d^3\mathbf{y}_2. \end{aligned} \quad (38)$$

One should note that since f and $\bar{f}$ differ only by a τ independent term, the bar can be omitted from the rhs of (37) for $n \neq 0$.

In order to enhance comparison with standard expressions for ΔF_2 , we take only the dipole terms in the multipole expansion of the Coulomb factors in (38) around fixed centers in the two molecules.

Defining the second moment tensor

$$\chi_n = \int \int \mathbf{x}_1 \mathbf{x}_2 \chi_n(\mathbf{x}_1, \mathbf{x}_2) d^3\mathbf{x}_1 d^3\mathbf{x}_2 \quad (39)$$

and denoting by $T(\mathbf{R})$ the dipole-dipole interaction tensor, where $\mathbf{R}$ is the relative position vector of the two molecular centers, we have

$$-\beta\Delta F_2 = \frac{1}{2} \sum_{n=-\infty}^{\infty} \text{Tr}\{\chi_{an}T(R)\chi_{bn}T(R)\}. \quad (40)$$

Comparing this to the well known expression, which has been derived repeatedly in recent years,⁷ for the second order van der Waals interaction energy of a pair of molecules at finite temperatures

$$-\beta\Delta F_2 = \frac{1}{2} \sum_{n=-\infty}^{\infty} \text{Tr}\{\chi_a(i\omega_n)T(R)\chi_b(i\omega_n)T(R)\} \quad (41)$$

we see that (40) and (41) will coincide if we can identify the coefficients χ_n with the dynamic susceptibility $\chi(i\omega_n)$ at the given imaginary frequency

$$\chi_n = \chi(i\omega_n) \quad (42)$$

with ω_n defined by (36), or equally, if we can identify the coefficients $\chi_n(x_1, x_2)$ in (38) with the dynamic mutual susceptibility⁸ $\chi_n(x_1, x_2, i\omega_n)$ at the given imaginary frequency:

$$\chi_n(\mathbf{x}_1, \mathbf{x}_2) = \chi(\mathbf{x}_1, \mathbf{x}_2, i\omega_n). \quad (43)$$

Note that a relation analogous to (37) holds between the coefficients χ_n defined in (39) and the dipole-dipole correlation function

$$\bar{f}(\tau) = \langle T\{\mu(\tau)\mu(0)\} \rangle \quad (44)$$

defined in terms of the dipole moment operators

$$\mu(\tau) = \int \mathbf{x} \bar{\rho}(\mathbf{x}) d^3\mathbf{x}. \quad (45)$$

The equalities (42) and (43) can be demonstrated by utilizing the formal connection between the general real time displaced correlation function

$$\phi(t) = \langle A(it)B(0) \rangle, \quad (46)$$

where for any operator A and any complex variable u we define

$$A(u) = e^{uH} A e^{-uH}, \quad (47)$$

and the correlation function

$$f(\tau) = \langle T\{A(\tau)B(0)\} \rangle \quad (48)$$

of the type of the functions defined in (28), (33), and (44) but with the extension to complex τ variables.⁹ The ordering operation T now stands for an ordering of operators according to decreasing values of the real parts of the τ . With the aid of the extended definition (48) of $f(\tau)$ we can write down now an expression for the response function, or after effect function, $\Phi(t)$ corresponding to the correlation function $\phi(t)$. We have, namely,

$$\phi(t) = f(it + \epsilon), \quad (49)$$

$$\phi(t)^* = \langle B(0)A(it) \rangle = f(it - \epsilon), \quad (50)$$

and (putting $\hbar = 1$)

$$\Phi(t) = i\{\phi(t) - \phi(t)^*\} = i\{f(it + \epsilon) - f(it - \epsilon)\}. \quad (51)$$

The corresponding susceptibility is given then by

$$\chi_+(\omega) = \int_0^\infty \Phi(t) e^{i\omega t} dt = i \int_0^\infty e^{i\omega t} f(it + \epsilon) dt - i \int_0^\infty e^{i\omega t} f(it - \epsilon) dt. \quad (52)$$

The two integrals in (52) can be joined into a single integral taken along the path C_+ in the complex τ plane (see Fig. 1)

$$\chi_+(\omega) = \int_{C_+} f(\tau) e^{\omega\tau} d\tau. \quad (53)$$

To insure convergence we must have necessarily $\text{Im}\omega > 0$. A corresponding analytic function of ω , $\chi_-(\omega)$, defined from $\text{Im}\omega < 0$ is given by

$$\chi_-(\omega) = \int_0^\infty \Phi(t) e^{i\omega t} dt \quad (54)$$

and can be brought to a form identical with (53) except that the integration path is replaced by C_- (see Fig. 1) which is a reflection of C_+ through the real τ axis. The two definitions can be combined to characterize the susceptibility $\chi(\omega)$ defined in the whole ω plane (except on the real ω axis itself) and consisting of the two analytic pieces $\chi_+(\omega)$ and $\chi_-(\omega)$.

If we replace ω by the purely imaginary variable $i\omega$, we have

$$\chi(i\omega) = \int_{C_+} f(\tau) e^{i\omega\tau} d\tau, \quad \omega \geq 0. \quad (55)$$

We make now use of the periodicity^{8(b)} of $f(\tau)$ with period β within the strip

$$-\beta < \text{Re}\tau < \beta. \quad (56)$$

If we choose for ω the sequence of values ω_n given

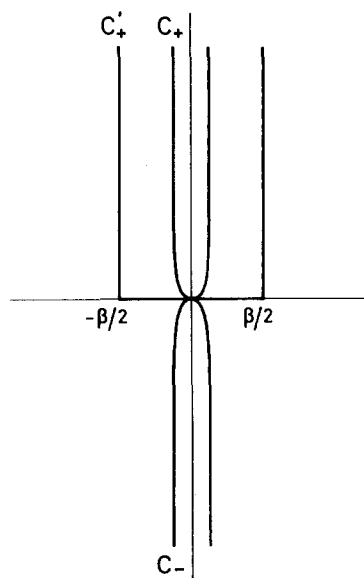


FIG. 1. Integration paths in complex τ plane.

in (36) the whole integrand in (55) is periodic with period β and we can deform the path C_+ into C'_+ as shown in Fig. 1 so that the integrals along the two vertical sections of C'_+ cancel each other and we are left with

$$\chi(i\omega_n) = \int_{-\beta/2}^{\beta/2} f(\tau) e^{i\omega_n \tau} d\tau. \quad (57)$$

This, however, is precisely the expression for the Fourier coefficient χ_n in the Fourier expansion

$$f(\tau) = \beta^{-1} \sum_{n=-\infty}^{\infty} \chi_n e^{-i\omega_n \tau}. \quad (58)$$

Thus, we have proved a general relation of which (42) and (43) are two special cases. With this we have concluded our demonstration that the expansion (17) indeed gives the familiar first and second order free energy of interaction of a pair of molecules.

APPENDIX

The operator H (in contrast to H_0) is completely symmetric with respect to electrons exchange. Hence if

$$A = \sum_P (\text{sgn} P) P \quad (A1)$$

is an antisymmetrizer, with the sum extended over some group of permutations of order N , H commutes with A [and with each term in (A1) alone].

Let F be the space of function acted on by H and S be the subspace of antisymmetric functions in F . We choose a complete orthonormal basis set $\{|s\rangle\}$ spanning S and write for the restricted trace of $e^{-\beta H}$ in S

$$\text{Tr}_S e^{-\beta H} = \sum_s \langle s | e^{-\beta H} | s \rangle. \quad (A2)$$

The set $\{|s\rangle\}$ can be augmented by an additional set $\{|\bar{s}\rangle\}$ of vectors orthonormal to S so that

$$\{|m\rangle\} \equiv \{|s\rangle\} + \{|\bar{s}\rangle\} \quad (A3)$$

forms an orthonormal basis set spanning the complete space F . Now the operator $N^{-1}A$ is a projector on the subspace S , hence

$$N^{-1}A |s\rangle = |s\rangle, \quad N^{-1}A |\bar{s}\rangle = 0, \quad (A4)$$

so that we can write for (A2)

$$\begin{aligned} \text{Tr}_S e^{-\beta H} &= \sum_s \langle s | e^{-\beta H} N^{-1}A | s \rangle \\ &\quad + \sum_{\bar{s}} \langle \bar{s} | e^{-\beta H} N^{-1}A | \bar{s} \rangle \\ &= N^{-1} \sum_m \langle m | e^{-\beta H} A | m \rangle = N^{-1} \text{Tr} e^{-\beta H} \end{aligned} \quad (A5)$$

and by the last equality in (A5) we can change over to any nonsymmetric complete orthonormal set in F and express in terms of it the last trace in (A5).

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⁹Much of the following is given essentially in Ref. 6(b).