CHAPTER V

THE POLARON AT FINITE TEMPERATURES

Until now, most of the polaron problems which have been studied by many authors are restricted to the case of absolute zero temperature. The more general case of polaron state at finite temperatures will be considered in this chapter. The polaron theory given in Chapter III, will now be reformulated so as to be applicable also to the case of finite temperatures.

V.1 The Polaron Action

We must first determine the polaron action at finite temperatures. According to Chapter II, the density matrix for the canonical ensemble is related to the propagator, and the canonical partition function can be written as

$$Z = \int d\underset{\sim}{r}_{el}\, \rho(\underset{\sim}{r}_{el}, \underset{\sim}{r}_{el}; \beta) = \int d\underset{\sim}{r}_{el}\, K(\underset{\sim}{r}_{el}, -i\hbar\beta; \underset{\sim}{r}_{el}, 0). \qquad (5.1)$$

For the polaron system, the propagator can be separated into the electron and the phonon parts. The partition function is then given by

$$Z = \int d\underset{\sim}{r}_{el} \int \mathcal{D}\underset{\sim}{r}_{el}(\tau)\, e^{-\frac{1}{2}\int_0^\beta \left(\frac{d\underset{\sim}{r}_{el}}{d\tau}\right)^2 d\tau} \prod_{\underset{\sim}{k}} \int dq_{\underset{\sim}{k}}\, K(q_{\underset{\sim}{k}}, \beta; q_{\underset{\sim}{k}}, 0), \qquad (5.2)$$

where we have used the imaginary time $\tau = it$, $\hbar = 1$, and the integration is over all paths $\underset{\sim}{r}_{el}(\tau)$ from $\underset{\sim}{r}_{el}$ back to $\underset{\sim}{r}_{el}$.

The propagator $K(q_{\underset{\sim}{k}}, \beta\,; q_{\underset{\sim}{k}}, 0)$ can be obtained from (3.16) and (3.17) by letting $t' = 0$ and $t'' = -i\beta$, thus

$$K(q_{\underset{\sim}{k}}, \beta\,; q_{\underset{\sim}{k}}, 0) = \left(\frac{m\omega_L}{2\pi \sinh \beta\omega_L}\right)^{\frac{1}{2}} \exp\left(iS_{cl}^{\underset{\sim}{k}}\right) \qquad (5.3)$$

where

$$\begin{aligned} S_{cl}^{\underset{\sim}{k}} &= -\frac{m\omega_L}{2i \sinh \beta\omega_L}\Bigg[2q_{\underset{\sim}{k}}^2 \cosh \omega_L \beta - 2q_{\underset{\sim}{k}}^2 + \frac{2q_{\underset{\sim}{k}}}{m\omega_L}\int_0^{-i\beta} dt\, \Gamma_{\underset{\sim}{k}}(t)\left(\sin\omega_L t - \sin\omega_L(i\beta - t)\right) \\ &\quad + \frac{2}{m^2\omega_L^2}\int_0^{t''} dt\, \Gamma_{\underset{\sim}{k}}(t) \sin\omega_L(i\beta + t)\int_0^{t} ds\, \Gamma_{\underset{\sim}{k}}(s) \sin\omega_L s \Bigg] \\ &= -\frac{m\omega_L}{2i \sinh \beta\omega_L}\Bigg[2(\cosh\beta\omega_L - 1)q_{\underset{\sim}{k}}^2 - \frac{2q_{\underset{\sim}{k}}}{m\omega_L}\int_0^{\beta} d\tau\, \Gamma_{\underset{\sim}{k}}(\tau)\left(\sinh\omega_L\tau + \sinh\omega_L(\beta - \tau)\right) \\ &\quad - \frac{2}{m^2\omega_L^2}\int_0^{\beta} d\tau \int_0^{\tau} d\sigma\, \Gamma_{\underset{\sim}{k}}(\tau)\Gamma_{\underset{\sim}{k}}(\sigma) \sinh\omega_L\tau \sinh\omega_L(\beta - \sigma)\Bigg], \qquad (5.4) \end{aligned}$$

where we have substituted $is = \sigma$.

The integration of the propagator is

$$\begin{aligned} \int dq_{\underset{\sim}{k}} K(q_{\underset{\sim}{k}}, \beta\,; q_{\underset{\sim}{k}}, 0) &= \left(\frac{m\omega_L}{2\pi \sinh\beta\omega_L}\right)^{\frac{1}{2}} \exp\left\{\frac{1}{m\omega_L \sinh\beta\omega_L}\int_0^{\beta}\int_0^{\tau} d\tau\, d\sigma\, \Gamma_{\underset{\sim}{k}}(\tau)\Gamma_{\underset{\sim}{k}}(\sigma) \sinh\omega_L\tau \sinh\omega_L(\beta-\sigma)\right\} \times \\ &\quad \int dq_{\underset{\sim}{k}} \exp\left\{-\frac{m\omega_L}{2\sinh\beta\omega_L}\left[2(\cosh\beta\omega_L - 1)q_{\underset{\sim}{k}}^2 - \frac{2q_{\underset{\sim}{k}}}{m\omega_L}\int_0^{\beta} d\tau\, \Gamma_{\underset{\sim}{k}}(\tau)\left(\sinh\omega_L\tau + \sinh\omega_L(\beta - \tau)\right)\right]\right\}, \\ &= \left(2\sinh\frac{\beta\omega_L}{2}\right)^{-1} \exp\left\{\frac{1}{2m\omega_L \sinh\beta\omega_L(\cosh\beta\omega_L - 1)}\int_0^{\beta}\int_0^{\beta} d\tau\, d\sigma\, \Gamma_{\underset{\sim}{k}}(\tau)\Gamma_{\underset{\sim}{k}}(\sigma) A\right\}, \qquad (5.5) \end{aligned}$$

where

$$\begin{aligned} A &= 2\sinh\omega_L\tau \sinh\omega_L(\beta - \sigma)(\cosh\beta\omega_L - 1) + \sinh\omega_L\tau \sinh\omega_L\sigma + \sinh\omega_L(\beta - \tau) \\ &\quad \cdot \sinh\omega_L\sigma + \sinh\omega_L \sinh\omega_L(\beta - \sigma) + \sinh\omega_L(\beta - \tau)\sinh\omega_L(\beta - \sigma), \end{aligned}$$

$$A = \frac{1}{4}\left[e^{\omega_L(\tau-\sigma)}(\bar{n}+1)+e^{-\omega_L(\tau-\sigma)}.\bar{n}\right](e^{2\omega_L\beta}-e^{-2\omega_L\beta}+2e^{-\omega_L\beta}-2e^{\omega_L\beta}) ,$$

and $\bar{n} = \dfrac{1}{e^{\omega_L\beta}-1}$, the average number of phonons in the k^{th} mode.

By substituting A into (5.5), we obtain

$$\int dq_{\underset{\sim}{k}} K(q_{\underset{\sim}{k}},\beta;q_{\underset{\sim}{k}},0) = \left(2\sinh\frac{\beta\omega_L}{2}\right)^{-1}\exp\left\{\frac{1}{2m\omega_L}\int_0^\beta\int_0^\tau d\tau\, d\sigma\, \Gamma_{\underset{\sim}{k}}(\tau)\Gamma_{\underset{\sim}{k}}(\sigma)\left[\bar{n}e^{\omega_L(\tau-\sigma)}+(\bar{n}+1)e^{-\omega_L(\tau-\sigma)}\right]\right\}. \tag{5.6}$$

Therefore the canonical partition function (5.2) becomes

$$Z = Z_{ph}V\int \mathcal{D}\underset{\sim}{r}_{el}(\tau)\, e^{-\frac{1}{2}\int_0^\beta\left(\frac{dr_{el}}{d\tau}\right)^2 d\tau} \exp\left\{\frac{1}{2m\omega_L}\int_0^\beta\int_0^\tau d\tau\, d\sigma\sum_{\underset{\sim}{k}}\Gamma_{\underset{\sim}{k}}(\tau)\Gamma_{\underset{\sim}{k}}(\sigma)\left[\bar{n}e^{\omega_L(\tau-\sigma)}+(\bar{n}+1)e^{-\omega_L(\tau-\sigma)}\right]\right\},$$

where the path integral does not depend on $\underset{\sim}{r}_{el}$, the integration of $\underset{\sim}{r}_{el}$ gives just the volume V, and $Z_{ph} = (2\sinh\frac{\beta\omega_L}{2})^{-N}$ is the partition function for the system of phonons in the absence of the electron. Recalling the value of $\sum_{\underset{\sim}{k}}\Gamma_{\underset{\sim}{k}}(\tau)\Gamma_{\underset{\sim}{k}}(\sigma)$ and α from (3.32) and (3.33), we obtain

$$Z = Z_{ph}V\int \mathcal{D}\underset{\sim}{r}_{el}(\tau)\, e^{-\frac{1}{2}\int_0^\beta\left(\frac{d\underset{\sim}{r}_{el}}{d\tau}\right)^2 d\tau+\frac{\alpha}{2^{3/2}}\int_0^\beta\int_0^\beta d\tau d\sigma\frac{\left[\bar{n}e^{|\tau-\sigma|}+(\bar{n}+1)e^{-|\tau-\sigma|}\right]}{|\underset{\sim}{r}_{el}(\tau)-\underset{\sim}{r}_{el}(\sigma)|}} , \tag{5.7}$$

where our units are such that $\hbar$, ω_L and m are unity.

Therefore the polaron action at finite temperatures is given by

$$S = -\frac{1}{2}\int_0^\beta\left(\frac{d\underset{\sim}{r}_{el}}{dt}\right)^2 dt+\frac{\alpha}{2^{3/2}}\left\{\frac{e^\beta}{e^\beta-1}\int_0^\beta\int dt\,ds\frac{e^{-|t-s|}}{|\underset{\sim}{r}_{el}(t)-\underset{\sim}{r}_{el}(s)|}+\frac{1}{e^\beta-1}\int_0^\beta\int dt\,ds\frac{e^{|t-s|}}{|\underset{\sim}{r}_{el}(t)-\underset{\sim}{r}_{el}(s)|}\right\} , \tag{5.8}$$

where the time variables τ and σ are replaced by t and s.

Now the polaron, after the phonons have been averaged out, is described by the action (5.8). The electron is in the coulomb potential with the energy depending on the average number of the phonons arising from the temperature dependence. Unfortunately, we cannot perform the path integration on S since only quadratic actions lead to integrable path integrals. We must choose an appropriate trial action that is integrable and which imitates the exact action S in rough approximation. The natural choice for the trial action , by analogy with that of the polaron state at absolute zero temperature, is given by Osaka as

$$S_1 = -\frac{1}{2}\int_0^\beta \left(\frac{d\underset{\sim}{r}_{el}}{dt}\right)^2 dt - \frac{c}{2}\left\{\frac{e^{\beta\omega}}{e^{\beta\omega}-1}\iint_0^\beta dt\,ds\,|\underset{\sim}{r}_{el}(t)-\underset{\sim}{r}_{el}(s)|^2 e^{-\omega|t-s|} + \frac{1}{e^{\beta\omega}-1}\iint_0^\beta dt\,ds \times \right.$$
$$\left. |\underset{\sim}{r}_{el}(t)-\underset{\sim}{r}_{el}(s)|^2\, e^{\omega|t-s|}\right\} . \qquad (5.9)$$

The kinetic energy part is the same as that of the exact action (5.8) and the potential terms resemble the harmonic oscillator potential with two adjustable variational parameters C and ω.

We shall now deal with the density matrix for the reason that it is closely related to the partition function. The density matrix of the polaron is given by

$$\rho(\underset{\sim}{r}_{el}, \underset{\sim}{r}'_{el}; \beta) = \int_0^\beta \mathcal{D}\underset{\sim}{r}_{el}(t)\exp S , \qquad (5.10)$$

where the path integration goes over all paths $\underset{\sim}{r}_{el}(t)$ from $\underset{\sim}{r}_{el}$ to $\underset{\sim}{r}'_{el}$ with the boundary conditions $\underset{\sim}{r}_{el}(0) = \underset{\sim}{r}_{el}$ and $\underset{\sim}{r}_{el}(\beta) = \underset{\sim}{r}'_{el}$. Hence,

$$\rho(\underset{\sim}{r}_{el}, \underset{\sim}{r}'_{el}; \beta) = \frac{\int_0^\beta \mathcal{D}\underset{\sim}{r}_{el}(t)\exp(S-S_1)\exp S_1}{\int_0^\beta \mathcal{D}\underset{\sim}{r}_{el}(t)\exp S_1} \cdot \int_0^\beta \mathcal{D}\underset{\sim}{r}_{el}(t)\exp S_1 ,$$

$$\rho(\underset{\sim}{r}_{el}, \underset{\sim}{r}'_{el}; \beta) = \langle \exp(S-S_1)\rangle \rho_{S_1}(\underset{\sim}{r}_{el}, \underset{\sim}{r}'_{el}; \beta)$$

$$\geq \rho_{tr}(\underset{\sim}{r}_{el}, \underset{\sim}{r}'_{el}; \beta) \quad , \qquad (5.11)$$

where $\rho_{tr}(\underset{\sim}{r}_{el}, \underset{\sim}{r}'_{el}; \beta) = \exp\langle S-S_1\rangle \rho_{S_1}(\underset{\sim}{r}_{el}, \underset{\sim}{r}'_{el}; \beta)$. (5.12)

Thus we obtain the variational principle according to which the trial density matrix (5.12) would be minimized with respect to the parameters C and ω. In order to calculate the value of ρ_{tr}, we need to evaluate $\langle S - S_1 \rangle$. This implies the explicit solution of the integro-differential equation, as already discussed in Chapter III and IV.

V.2 Model Lagrangian

To determine $\langle S - S_1 \rangle$ in the present case, we must solve the integro-differential equation which is even more complicated than that considered in Chapter III for the polaron at absolute zero temperature. In order to avoid this difficulty, we shall now consider the model Lagrangian introduced by Osaka, viz.,

$$L' = \frac{1}{2}\dot{\underset{\sim}{r}}^2 + \frac{1}{2}M\dot{\underset{\sim}{R}}^2 - \frac{k}{2}(\underset{\sim}{r} - \underset{\sim}{R})^2 \quad , \qquad (5.13)$$

where M and k have the dimensions of mass and force constant, respectively.

The polaron system described by the trial action S_1 can be represented by the model Lagrangian (5.13), the validity of which assumption will now be demonstrated. To accomplish this we shall first determine the classical path equation of motion by the trial action S_1. Since

$$\delta S_1 = 0 = -\frac{1}{2}\int_0^\beta 2\left(\frac{d\bar{\underset{\sim}{r}}_{el}(t)}{dt}\right)\delta\dot{\bar{\underset{\sim}{r}}}_{el}(t)dt - \frac{c}{2}\left\{\frac{e^{\beta\omega}}{e^{\beta\omega}-1}\,2\iint_0^\beta dt\,ds\left[\bar{\underset{\sim}{r}}_{el}(t)-\bar{\underset{\sim}{r}}_{el}(s)\right]\times\right.$$

$$e^{-\omega|t-s|}\,\delta\left[\bar{\underset{\sim}{r}}_{el}(t)-\bar{\underset{\sim}{r}}_{el}(s)\right]+\frac{1}{e^{\beta\omega}-1}\,2\iint_0^\beta dt\,ds\left[\bar{\underset{\sim}{r}}_{el}(t)-\bar{\underset{\sim}{r}}_{el}(s)\right]\times$$

$$\left. e^{\omega|t-s|}\,\delta\left[\bar{\underset{\sim}{r}}_{el}(t)-\bar{\underset{\sim}{r}}_{el}(s)\right]\right\}$$

$$=\int_0^\beta\left[\frac{d^2\bar{\underset{\sim}{r}}_{el}(t)}{dt^2}-2c\left\{\frac{e^{\beta\omega}}{e^{\beta\omega}-1}\int_0^\beta ds\left[\underset{\sim}{r}_{el}(t)-\underset{\sim}{r}_{el}(s)\right]e^{-\omega|t-s|}+\frac{1}{e^{\beta\omega}-1}\int ds\left[\underset{\sim}{r}_{el}(t)-\underset{\sim}{r}_{el}(s)\right]e^{\omega|t-s|}\right\}\right]\delta\bar{\underset{\sim}{r}}_{el}(t)dt,$$

it follows that

$$\frac{d^2\bar{\underset{\sim}{r}}_{el}(t)}{dt^2}=\frac{4c}{\omega}\,\bar{r}_{el}(t)-2c\int_0^\beta ds\left[\frac{e^{\beta\omega}}{e^{\beta\omega}-1}e^{-\omega|t-s|}+\frac{1}{e^{\beta\omega}-1}e^{\omega|t-s|}\right]\bar{\underset{\sim}{r}}_{el}(s)\,, \qquad (5.14)$$

where the equality

$$\frac{e^{\beta\omega}}{e^{\beta\omega}-1}\int_0^\beta ds\,e^{-\omega|t-s|}+\frac{1}{e^{\beta\omega}-1}\int_0^\beta ds\,e^{\omega|t-s|}=\frac{2}{\omega}\,,$$

has been used.

The density matrix $\rho_{S_1}(\underset{\sim}{r}_{el},\underset{\sim}{r}'_{el};\beta)$ can be determined by using (5.14) as

$$\rho_{S_1}(\underset{\sim}{r}_{el},\underset{\sim}{r}'_{el};\beta)=\int_0\mathcal{D}\underset{\sim}{r}_{el}(t)\exp\left[-\frac{1}{2}\int_0^\beta\left(\frac{d\underset{\sim}{r}_{el}}{dt}\right)^2dt-\frac{c}{2}\left\{\frac{e^{\beta\omega}}{e^{\beta\omega}-1}\iint_0 dt\,ds\,|\underset{\sim}{r}_{el}(t)-\underset{\sim}{r}_{el}(s)|^2e^{-\omega|t-s|}\right.\right.$$

$$\left.\left.+\frac{1}{e^{\beta\omega}-1}\iint_0 dt\,ds\,|\underset{\sim}{r}_{el}(t)-\underset{\sim}{r}_{el}(s)|^2e^{\omega|t-s|}\right]\right. . \qquad (5.15)$$

By using the Gaussian integral method, the path integration (5.15) can be performed .

Thus

$$\rho_{S_1}(\underset{\sim}{r}_{el}, \underset{\sim}{r}'_{el}; \beta) = \exp\left\{-\frac{1}{2}\int\left(\frac{d\bar{\underset{\sim}{r}}_{el}}{dt}\right)^2 dt - \frac{c}{2}\left[\frac{e^{\beta\omega}}{e^{\beta\omega}-1}\iint_0^\beta dt\,ds\,|\bar{\underset{\sim}{r}}_{el}(t)-\bar{\underset{\sim}{r}}(s)|^2 e^{-\omega|t-s|} + \frac{1}{e^{\beta\omega}-1}\,dt\,ds\,|\bar{\underset{\sim}{r}}_{el}(t)-\bar{\underset{\sim}{r}}_{el}(s)|^2 e^{\omega|t-s|}\right]\right\}. \tag{5.16}$$

By substituting $A = \frac{e^{\beta\omega}}{e^{\beta\omega}-1}e^{-\omega|t-s|} + \frac{1}{e^{\beta\omega}-1}e^{\omega|t-s|}$ and interchanging the imaginary time t and s , (5.16) becomes

$$\rho_{S_1}(\underset{\sim}{r}_{el}, \underset{\sim}{r}'_{el}; \beta) = \exp\left\{-\frac{1}{2}\dot{\bar{\underset{\sim}{r}}}_{el}(t)\bar{\underset{\sim}{r}}_{el}(t)\Big|_0^\beta + \frac{1}{2}\int_0^\beta \frac{d^2\bar{\underset{\sim}{r}}_{el}(t)}{dt^2}\cdot\bar{\underset{\sim}{r}}_{el}(t)\,dt - \frac{c}{2}\left[\iint_0^\beta dt\,ds\,|\bar{\underset{\sim}{r}}_{el}(t)|^2 A + \iint_0^\beta dt\,ds\,|\bar{\underset{\sim}{r}}_{el}(s)|^2 A - 2\iint_0^\beta dt\,ds\,\bar{\underset{\sim}{r}}_{el}(t)\bar{\underset{\sim}{r}}_{el}(s)\,A\right]\right\}$$

$$= \exp\left\{-\frac{1}{2}\left(\dot{\underset{\sim}{r}}_{el}(\beta)\cdot\underset{\sim}{r}_{el}(\beta) - \dot{\underset{\sim}{r}}_{el}(0)\cdot\underset{\sim}{r}_{el}(0)\right)\right\}. \tag{5.17}$$

The next purpose is to find the density matrix of the model Lagrangian L'. With substitution of $k\underset{\sim}{r} = \underset{\sim}{\Gamma}(t)$ into (5.13) we obtain

$$L' = \left(\frac{1}{2}\dot{\underset{\sim}{r}}^2 - \frac{1}{2}k\underset{\sim}{r}^2\right) + \left(\frac{1}{2}M\dot{\underset{\sim}{R}}^2 - \frac{1}{2}k\underset{\sim}{R}^2 + \underset{\sim}{\Gamma}(t)\underset{\sim}{R}\right), \tag{5.18}$$

where the second part of L' has the form of the forced harmonic oscillator Lagrangian. Therefore the density matrix of L' can be easily determined by using (5.6), thus

$$\rho'(\underset{\sim}{r}, \underset{\sim}{r}'; \beta) = \int \mathcal{D}\underset{\sim}{r}_{el}(\tau)\exp\left[-\frac{1}{2}\int_0^\beta\left(\left(\frac{d\underset{\sim}{r}(\tau)}{d\tau}\right)^2 + k\underset{\sim}{r}^2(\tau)\right)\right]\int_0^\beta d\underset{\sim}{R}\,K(\underset{\sim}{R},\beta;\underset{\sim}{R},0)$$

$$= \left(2\sinh\frac{\beta\omega'}{2}\right)^{-3}\int\exp\left[-\int_0^\beta\left(\frac{1}{2}\dot{\underset{\sim}{r}}^2 + \frac{k}{2}\underset{\sim}{r}^2\right)dt + \frac{M\omega^3}{4}\iint_0^\beta dt\,ds\,\underset{\sim}{r}(t)\underset{\sim}{r}(s)\left[\frac{e^{\beta\omega'}}{e^{\beta\omega'}-1}e^{-\omega'|t-s|} + \frac{1}{e^{\beta\omega'}-1}e^{\omega'|t-s|}\right]\right]\mathcal{D}\underset{\sim}{r}_{el}(t), \tag{5.19}$$

where t and s are imaginary times and $\omega' = \sqrt{k/M}$. The equation of motion of the classical path $\bar{\underset{\sim}{r}}(t)$ can be derived from the action of the above equation, viz,

$$S' = -\int_0^\beta (\tfrac{1}{2}\dot{\underset{\sim}{r}}^2 + \tfrac{k}{2}\underset{\sim}{r}^2)\,dt + \frac{M\omega_3'}{4}\iint_0^\beta dt\,ds\,\underset{\sim}{r}(t)\,\underset{\sim}{r}(s)\,A' \quad .$$

Therefore

$$\delta S' = 0 = -\dot{\bar{\underset{\sim}{r}}}\,\delta\bar{\underset{\sim}{r}}\Big|_0^\beta + \int_0^\beta (\ddot{\bar{\underset{\sim}{r}}}(t) - k\bar{\underset{\sim}{r}})\,\delta\bar{\underset{\sim}{r}}(t)\,dt + \frac{M\omega'^3}{2}\iint_0^\beta dt\,ds\,\bar{\underset{\sim}{r}}(s)\,\delta\bar{\underset{\sim}{r}}(t)\,A' \ ,$$

and hence

$$\ddot{\bar{\underset{\sim}{r}}}(t) = k\bar{\underset{\sim}{r}}(t) - \frac{M\omega'^3}{2}\int_0^\beta ds\,\bar{\underset{\sim}{r}}(s)\left\{\frac{e^{\beta\omega'}}{e^{\beta\omega'}-1}\,e^{-\omega'|t-s|} + \frac{1}{e^{\beta\omega'}-1}\,e^{\omega'|t-s|}\right\} . \qquad (5.20)$$

The density matrix (5.19) can now be determined by using the Gaussian integral method and (5.20); we then obtain

$$\rho'(\underset{\sim}{r},\underset{\sim}{r}';\beta) = \exp\left[-\int_0^\beta \left(\tfrac{1}{2}\dot{\bar{\underset{\sim}{r}}}^2(t) + k\bar{\underset{\sim}{r}}^2(t)\right)dt + \frac{M\omega'^3}{4}\iint_0^\beta dt\,ds\,\bar{\underset{\sim}{r}}(t)\,\bar{\underset{\sim}{r}}(s)\,A'\right]$$

$$= \exp\left[-\tfrac{1}{2}\left(\dot{\bar{\underset{\sim}{r}}}(\beta)\,\bar{\underset{\sim}{r}}(\beta) - \dot{\bar{\underset{\sim}{r}}}(0)\cdot\bar{\underset{\sim}{r}}(0)\right)\right] \ , \qquad (5.21)$$

under the boundary conditions $\bar{\underset{\sim}{r}}(\beta) = \underset{\sim}{r}'$ and $\underset{\sim}{r}(0) = \underset{\sim}{r}$.
If we put $\omega' = \omega$ and $M\omega'^3 = 4C$, (5.20) is then identical to (5.14); and if we further put $\underset{\sim}{r}' = \underset{\sim}{r}'_{el}$ and $\underset{\sim}{r} = \underset{\sim}{r}_{el}$, (5.21) is then the same as (5.17).

Consequently, we shall use the model Lagrangian instead of the trial action S_1 in the further calculation. That is, the path integral of the trial action S_1 will be replaced by the path integral of the Lagrangian L'.

V.3 Evaluation of the Polaron Energy

Our first objective is to determine $\langle S - S_1 \rangle$ in (5.12). It can be expressed as $\langle S - S_1 \rangle = \langle S \rangle - \langle S_1 \rangle$, where

$$\langle S \rangle = \frac{\alpha}{2^{3/2}} \iint_0^\beta dt\,ds \left\langle \frac{1}{|\underset{\sim}{r}_{el}(t) - \underset{\sim}{r}_{el}(s)|} \right\rangle \left\{ \frac{e^\beta}{e^\beta - 1} \cdot e^{-|t-s|} + \frac{1}{e^\beta - 1} \cdot e^{|t-s|} \right\} , \quad (5.22)$$

and

$$\langle S_1 \rangle = -\frac{C}{2} \iint_0^\beta dt\,ds \left\langle |\underset{\sim}{r}_{el}(t) - \underset{\sim}{r}_{el}(s)|^2 \right\rangle \left\{ \frac{e^{\beta\omega}}{e^{\beta\omega} - 1}\, e^{-\omega|t-s|} + \frac{1}{e^{\beta\omega} - 1}\, e^{\omega|t-s|} \right\} . \quad (5.23)$$

In order to calculate $\langle S \rangle$, it is necessary to determine $\left\langle \frac{1}{|\underset{\sim}{r}_{el}(t) - \underset{\sim}{r}_{el}(s)|} \right\rangle$ which can be expressed as a Fourier transform,

$$\left\langle \frac{1}{|\underset{\sim}{r}_{el}(t) - \underset{\sim}{r}_{el}(s)|} \right\rangle = \int_{-\infty}^{\infty} \frac{d^3\underset{\sim}{K}}{2\pi^2 K^2} \left\langle \exp[i\underset{\sim}{K} \cdot (\underset{\sim}{r}_{el}(t) - \underset{\sim}{r}_{el}(s))] \right\rangle . \quad (5.24)$$

It follows that we must evaluate $\left\langle \exp[\, i\underset{\sim}{K} \cdot (\underset{\sim}{r}_{el}(t) - \underset{\sim}{r}_{el}(s)] \right\rangle$.

Let us consider

$$\left\langle \exp[i\underset{\sim}{K} \cdot (\underset{\sim}{r}_{el}(\tau) - \underset{\sim}{r}_{el}(\sigma))] \right\rangle = \frac{\int \mathcal{D}\underset{\sim}{r}_{el}(t)\, \exp[\int f(t) \cdot \underset{\sim}{r}_{el}(t)\,dt]\, \exp S_1}{\int \mathcal{D}\underset{\sim}{r}_{el}(t)\, \exp S_1} , \quad (5.25)$$

where

$$f(t) = i\underset{\sim}{K}\,(\delta(t-\tau) - \delta(t-\sigma)) .$$

It is recalled that the path integration of the action S_1 can be replaced by that of the Lagrangian L'. Similarly the path integration of (5.25) can also be replaced by that of the following Lagrangian,

$$L = \frac{1}{2}\dot{\underset{\sim}{r}}^2 + \frac{1}{2} M\dot{\underset{\sim}{R}}^2 - \frac{k}{2}(\underset{\sim}{r} - \underset{\sim}{R})^2 + \underset{\sim}{f}(t) \cdot \underset{\sim}{r} . \quad (5.26)$$

Let us introduce the following new variables

$$\underset{\sim}{q} = \underset{\sim}{r} - \underset{\sim}{R} , \quad \underset{\sim}{Q} = \frac{\underset{\sim}{r} + M\underset{\sim}{R}}{1+M} , \quad (5.27)$$

then the Lagrangian (5.26) can be written as

$$L = \frac{1}{2}\left(\frac{M}{M+1}\right)\dot{\underset{\sim}{q}}^2 - \frac{k}{2}\underset{\sim}{q}^2 + \left(\frac{M}{M+1}\right)\underset{\sim}{f}(t)\cdot\underset{\sim}{q}(t) + \frac{1}{2}(M+1)\dot{\underset{\sim}{Q}}^2 + \underset{\sim}{Q}\cdot\underset{\sim}{f}(t). \qquad (5.28)$$

The classical path equation of motion for $\underset{\sim}{q}$ and $\underset{\sim}{Q}$ can be obtained from the principle of least action. We obtain

$$\ddot{\bar{\underset{\sim}{q}}} - \nu^2\bar{\underset{\sim}{q}} = -\underset{\sim}{f}(t) , \qquad (5.29a)$$

and

$$\ddot{\bar{\underset{\sim}{Q}}} = \frac{-\underset{\sim}{f}(t)}{M+1} , \qquad (5.29b)$$

where

$$v^2 = \frac{k(M+1)}{M} = \frac{4C}{\omega} + \omega^2 .$$

To solve (5.29a), we shall use the Green function method. The Green function equation that satisfies (5.29a) is

$$\left(\frac{d^2}{ds^2} - \nu^2\right) G(s,t) = \delta(s-t) , \qquad (5.30)$$

with the solution

$$G(s,t) = G_1(s,t)H(t-s) + G_2(s,t)H(s-t) ,$$

where $\quad G_1(s,t) = A \sinh vs + B \cosh vs ,$

and $\quad G_2(s,t) = A'\sinh vs + B'\cosh vs .$

The constants A, B, A', and B' are readily found, then we obtain

$$G(S,t) = -\frac{\sinh vt}{v}\left(\coth vt - \coth v\beta\right)\sinh vs\, H(t-s)$$

$$- \frac{\sinh vt}{v}\left(\cosh vs - \coth v\beta \sinh vs\right) H(t-s). \qquad (5.31)$$

From (5.29a) and (5.30), we have

$$\bar{\underset{\sim}{q}}(t) = \bar{\underset{\sim}{q}}(\beta)\, G(\beta,t) - \bar{\underset{\sim}{q}}(0)\, G(0,t) - \int_0^\beta \underset{\sim}{f}(s)\cdot G(s,t)\, dS , \qquad (5.32)$$

where G(s,t) is given by (5.31).

Then

$$
\begin{aligned}
\underset{\sim}{\bar{q}}(t) \quad = \quad & -q_{\delta_2} \frac{\sinh vt\,(\sinh^2 v\beta - \cosh^2 v\beta)}{\sinh v\beta} + q_{\delta_1} \sinh vt\,(\coth vt - \coth v\beta) \\
& - \int_0^t ds\, i\underset{\sim}{k}\left(\delta(t-\tau)-\delta(t-\sigma)\right)\left[-\frac{\sinh vt}{v}(\coth vt - \coth v\beta)\sinh vs\right] \\
& - \int_t^\beta ds\, i\underset{\sim}{k}\left(\delta(t-\tau)-\delta(t-\sigma)\right)\left[-\frac{\sinh vt}{v}(\cosh vs - \coth v\beta \sinh vs)\right] \\
= \quad & \left(q_{\delta_1} \sinh v(\beta-t) + q_{\delta_2} \sinh vt\right)/\sinh v\beta \\
& + i\underset{\sim}{k} \sinh vt\,\left(\sinh v(\beta-\tau) - \sinh v(\beta-\sigma)\right)/v\sinh v\beta \\
& - \frac{i\underset{\sim}{k}}{v}\left[\sinh v(t-\tau)H(t-\tau) - \sinh v(t-\sigma)H(t-\sigma)\right], \qquad (5.33)
\end{aligned}
$$

under the conditions $\underset{\sim}{\bar{q}}(0) = q_1$ and $\underset{\sim}{\bar{q}}(\beta) = q_2$.

To solve the differential equation (5.29b), we shall use the same method as that applied to (5.29a). Then we obtain

$$
\frac{d^2 G(s,t)}{ds^2} = \delta(s-t) \qquad , \qquad (5.34)
$$

with the solution

$$
G(s,t) = \frac{(t-\beta)}{\beta} . s\, H(t-s) + \frac{t}{\beta}(s-\beta)\, H(s-t). \quad (5.35)
$$

Eqs.(5.29b) and (5.34) lead to

$$
\begin{aligned}
\underset{\sim}{\bar{Q}}(t) \quad = \quad & \underset{\sim}{\bar{Q}}(\beta)\,\dot{G}(\beta,t) - \underset{\sim}{\bar{Q}}(0)\,\dot{G}(0,t) - \frac{1}{M+1}\int_0^\beta f(s)\,G(s,t)\,ds \\
= \quad & Q_1 + \left\{(Q_2 - Q_1) - i\underset{\sim}{k}\frac{\omega^2}{v^2}(\tau-\sigma)\right\}\frac{t}{\beta} - i\underset{\sim}{k}\frac{\omega^2}{v^2}\left\{(t-\tau)H(t-\tau) - (t-\sigma)H(t-\sigma)\right\}. \\
& \qquad (5.36)
\end{aligned}
$$

under the conditions $\underset{\sim}{\bar{Q}}(\beta) = Q_2$ and $\underset{\sim}{\bar{Q}}(0) = Q_1$.

The equation (5.25) can now be evaluated by using (5.29a,b) and the path integration can be carried out by using the Gaussian integral method. We thus obtain

$$
\begin{aligned}
\left\langle \exp\left[i\underset{\sim}{K}\cdot\left(\underset{\sim}{r}_{el}(\tau)-\underset{\sim}{r}_{el}(\sigma)\right)\right]\right\rangle_{\substack{Q_1,q_1\\ Q_2,q_2,\beta}} &= \exp\left\{\int_0^\beta \left[-\frac{1}{2}\left(\frac{M}{M+1}\right)\dot{\bar{\underset{\sim}{q}}}^2-\frac{K}{2}\left(\frac{M}{M+1}\right)\underset{\sim}{f}(t)\cdot\bar{\underset{\sim}{q}}\right.\right.\\
&\qquad \left.\left. -\frac{(M+1)}{2}\dot{\bar{\underset{\sim}{Q}}}^2+\bar{\underset{\sim}{Q}}\cdot f(t)\right]dt\right\}\\
&= \exp\left\{-\frac{M}{2(M+1)}\left[\dot{\bar{\underset{\sim}{q}}}(\beta)q_2-\dot{\bar{\underset{\sim}{q}}}(0)q_1\right]+i\underset{\sim}{K}\frac{M}{2(M+1)}\left(\bar{q}(\tau)-\bar{q}(\sigma)\right)\right.\\
&\qquad \left. -\frac{M+1}{2}\left[\dot{\bar{\underset{\sim}{Q}}}(\beta)Q_2-\dot{\bar{\underset{\sim}{Q}}}(0)Q_1\right]+i\underset{\sim}{K}\cdot\frac{1}{2}\left(\bar{\underset{\sim}{Q}}(\tau)-\bar{\underset{\sim}{Q}}(\sigma)\right)\right\}. \qquad (5.37)
\end{aligned}
$$

We can determine (5.37) by using (5.33) and (5.36). In order to connect the variables in the Lagrangian L with that in the action S_1, we replace the variables Q_1, q_1 and Q_2, q_2 in the above equation with r_1, R_1 and r_2, R_2. Then, integrating (5.37) with respect to the variable R_1, under the condition $R_2 = R_1$, we obtain

$$
\begin{aligned}
\left\langle \exp\left[i\underset{\sim}{K}\cdot\left(\underset{\sim}{r}_{el}(\tau)-\underset{\sim}{r}_{el}(\sigma)\right)\right]\right\rangle_{r_1,r_1} &= \int_{-\infty}^{\infty} \exp\left\{-\frac{M}{2(M+1)}\left[2(r_1^2-2r_1R_1+R_1^2)\frac{v(\cosh v\beta-1)}{\sinh v\beta}\right.\right.\\
&\qquad +\frac{i\underset{\sim}{K}}{\sinh v\beta}(r_1-R_1)\left\{(\sinh v(\beta-\tau)-\sinh v(\beta-\sigma)(\cosh v\beta-1)\right.\\
&\qquad -\left(\cosh v(\beta-\sigma)-\cosh v(\beta-\sigma)\right)\sinh v\beta\\
&\qquad -(\sinh v(\beta-\tau)-\sinh v(\beta-\sigma)+\sinh v\tau\\
&\qquad \left.\left.\left. -\sinh v\sigma)\right\}\right]\right\}\cdot\\
&\qquad \exp\left\{-\frac{M}{2(M+1)}\left[\frac{K^2}{v\sinh v\beta}(\sinh v\tau-\sinh v\sigma)\left(\sinh(v)(\beta-\tau)-\sinh v(\beta-\sigma)\right)\right.\right.\\
&\qquad \left.\left. +\frac{K^2}{v}\sinh v|\tau-\sigma|\right]+\frac{K^2\omega^2}{2v^2}\cdot\frac{|\tau-\sigma|^2}{\beta}-\frac{K^2\omega^2}{2v^2}|\tau-\sigma|\right\}dR_1,\\
&= \exp\left\{F(\tau,\sigma,\beta)\right\}\int_{-\infty}^{\infty}\exp\left\{-\frac{M}{2(M+1)}\left[Ar_1^2+Br_1+AR_1^2-R_1(2Ar_1+B)\right]\right\}dR_1,
\end{aligned}
$$

(5.38)

where

$$F(\tau,\sigma,\beta) = -\frac{M}{2(M+1)}\left[\frac{K^2}{v\sinh v\beta}(\sinh v\tau - \sinh v\sigma)(\sin v(\beta-\tau) - \sinh v(\beta-\sigma)) + \frac{K^2}{v}\sinh v|\tau-\sigma|\right] + \frac{K^2\omega^2}{2v^2}\cdot\frac{|\tau-\sigma|^2}{\beta} - \frac{K^2\omega^2}{2v^2}|\tau-\sigma|, \quad (5.38a)$$

$$A = \frac{2v}{\sinh v\beta}(\cosh v\beta - 1), \quad (5.38b)$$

and

$$B = \frac{iK}{\sinh v\beta}\Big\{(\sinh v(\beta-\tau) - \sinh v(\beta-\sigma)(\cosh v\beta - 1) - (\cosh v(\beta-\tau) - \cosh v(\beta-\sigma))\sinh v\beta - (\sinh v(\beta-\tau) - \sinh v(\beta-\sigma) + \sinh v\tau - \sinh v\sigma)\Big\}. \quad (5.38c)$$

The integration of (5.38) can be easily performed by using

$$\int_{-\infty}^{\infty} e^{ax^2+bx}\,dx = \sqrt{\frac{\pi}{a}}\, e^{-b^2/4a}$$; then we obtain

$$\langle \exp[i\underset{\sim}{K}\cdot(\underset{\sim el}{r}(\tau) - \underset{\sim el}{r}(\sigma))]\rangle_{r_1, r_1} = \exp\{F(\tau,\sigma,\beta)\}\exp\Big\{-\frac{M}{2(M+1)}(Ar_1^2 + Br_1)\Big\}\sqrt{\frac{\pi}{A\frac{M}{2(M+1)}}}\exp\Big\{\frac{M}{2(M+1)}\frac{(2Ar_1+B)^2}{4A}\Big\}$$

$$= \sqrt{\frac{\pi}{A\frac{M}{(M+1)}}}\cdot\exp\Big\{-\frac{M}{2(M+1)}\Big[\frac{K^2}{v\sinh v\beta}(\sinh v\tau - \sinh v\sigma)(\sinh v(\beta-\tau) - \sinh v(\beta-\sigma)) + \frac{K^2}{v^2}\sinh v|\tau-\sigma| - \frac{2(M+1)}{M}\Big(\frac{K^2\omega^2}{2v^2}\cdot\frac{|\tau-\sigma|^2}{\beta} - \frac{K^2\omega^2}{2v}|\tau-\sigma|\Big) + \frac{K^2}{v}(\cosh v|\tau-\sigma|-1)\coth\frac{v\beta}{2}\Big[\cosh v(\beta - \frac{\tau+\sigma}{\tau}) - \cosh v\frac{|\tau-\sigma|}{2}\Big]^2 \Big/ 4\sinh^2\frac{v\beta}{\tau}\cosh^2\frac{v\beta}{\tau}\Big]\Big\}$$

$$= \sqrt{\frac{\pi}{A\frac{M}{(M+1)}}}\exp\Big\{-K^2\Big[\frac{2c}{v3\omega}\Big\{(1-e^{-v|\tau-\sigma|}) + (1-\coth\frac{v\beta}{2})(\cosh v|\tau-\sigma|-1)\Big\} + \frac{\omega^2}{2v^2}|\tau-\sigma|\Big(1 - \frac{|\tau-\sigma|}{\beta}\Big)\Big]\Big\}. \quad (5.39)$$

Since the right hand side of the above equation is independent of the boundary condition, the suffix r_1, r_1 associated with the averaging can be omitted. We obtain

$$\left\langle \exp\left[i\underset{\sim}{K}\cdot(\underset{\sim el}{r}(\tau)-\underset{\sim el}{r}(\sigma))\right]\right\rangle = \exp\left\{-K^2\left[\frac{2c}{v^3\omega}\left\{(1-e^{-|\tau-\sigma|})+(1-\coth\frac{v\beta}{2})(\cosh v|\tau-\sigma|-1)\right\}\right.\right.$$

$$\left.\left.+\frac{\omega^2}{2v^2}|\tau-\sigma|\left(1-\frac{|\tau-\sigma|}{\beta}\right)\right]\right\}, \qquad (5.40)$$

where the fact that $\left\langle \exp\left[i\underset{\sim}{K}\cdot(\underset{\sim}{r}_{el}(\tau)-\underset{\sim}{r}_{el}(\sigma))\right]\right\rangle$ becomes unity in the case of $\underset{\sim}{K}$ tending to zero has been used.

Now the average of the polaron action can be obtained by using (5.22), (5.24), and (5.40),

$$\langle S\rangle = \frac{\alpha}{2^{3/2}}\iint_0^\beta dt\,ds\int_{-\infty}^{\infty}\frac{d^3\underset{\sim}{K}}{2\pi^2K^2}\exp\left\{-K^2\left[\frac{2c}{v^3\omega}\left\{(1-e^{-v|t-s|})+(1-\coth\frac{v\beta}{2})(\cosh v|t-s|-1)\right\}\right.\right.$$

$$\left.\left.+\frac{\omega^2}{2v^2}|t-s|\left(1-\frac{|t-s|}{\beta}\right)\right]\right\}\times$$

$$\left\{\frac{e^\beta}{e^\beta-1}e^{-|t-s|}+\frac{1}{e^\beta-1}e^{|t-s|}\right\}. \qquad (5.41)$$

After performing the integration on K, we obtain

$$\langle S\rangle = \frac{\alpha}{\pi^{1/2}}v\beta\int_0^\beta d\tau\left\{\frac{e^\beta}{e^\beta-1}e^{-\tau}+\frac{1}{e^\beta-1}e^{\tau}\right\}\left[\frac{(v^2-\omega^2)}{v}\left\{(1-e^{-v\tau})+(1-\coth v\beta)\times\right.\right.$$

$$\left.\left.(\cosh v\tau-1)\right\}+\omega^2\tau\left(1-\frac{\tau}{\beta}\right)\right]^{-\frac{1}{2}}. \qquad (5.42)$$

The next object is to find $\langle S_1\rangle$. We must first determine $\left\langle |r_{el}(\tau)-r_{el}(\sigma)|^2\right\rangle$ and then substitute the result in (5.23). To accomplish this, we apply the second order differentiation to (5.40), thus

$$\langle|\underset{\sim el}{r}(\tau)-\underset{\sim el}{r}(\sigma)|^2\rangle = 3\left[\frac{v^2-\omega^2}{v^2}\left\{(1-e^{-v|\tau-\sigma|})+(1-\coth\frac{v\beta}{2})(\cosh v|\tau-\sigma|-1)\right\}\right.$$

$$\left.+\frac{\omega^2}{v^2}|\tau-\sigma|\left(1-\frac{|\tau-\sigma|}{\beta}\right)\right]. \qquad (5.43)$$

Hence

$$\langle S_1\rangle = -\frac{3C}{2}\iint_0^{\beta} dt\,ds\Big[\frac{(v^2-\omega^2)}{v^3}\Big\{(1-e^{-v|t-s|})+(1-\coth\frac{v\beta}{2})(\cosh v|t-s|-1)\Big\}$$

$$+\frac{\omega^2}{v^2}|t-s|(1-\frac{|t-s|}{\beta})\Big]\Big\{\frac{e^{\beta\omega}}{e^{\beta\omega}-1}e^{-\omega|t-s|}+\frac{1}{e^{\beta\omega}-1}e^{\omega|t-s|}\Big\}$$

$$= -\frac{3C\beta}{v\omega}\Big(\coth\frac{v\beta}{2}-\frac{2}{v\beta}\Big) \qquad (5.44)$$

Since the free energy can be expressed in terms of the canonical partition function and the diagonal density matrix as

$$F = -\frac{1}{\beta}\ln Z ,$$

$$Z = \int_{-\infty}^{\infty}\rho(\underset{\sim}{r}_{el},\underset{\sim}{r}_{el};\beta)\,d\underset{\sim}{r}_{el} ,$$

then the trial free energy is given by

$$F_{tr} = -\frac{1}{\beta}\ln\int_{-\infty}^{\infty}\exp\langle S-S_1\rangle\,\rho_{S_1}(\underset{\sim}{r}_{el},\underset{\sim}{r}_{el};\beta)\,d\underset{\sim}{r}_{el}$$

$$= -\frac{\langle S-S_1\rangle}{\beta}-\frac{\ln Z_{S_1}}{\beta} , \qquad (5.45)$$

where Z_{S_1} is the partition function derived from the density matrix $\rho_{S_1}(\underset{\sim}{r}_{el},\underset{\sim}{r}_{el};\beta)$. The second term of the free energy (5.45) can be derived from the relation

$$\frac{\delta\ln Z_{S_1}}{\delta C} = \frac{\langle S_1\rangle}{C} , \qquad (5.46)$$

which is derived from the definitions of $\ln Z_{S_1}$ and $\langle S_1\rangle$. By performing the integration on (5.46) and transforming the variable C in the integral term of $\langle S_1\rangle$ into the term of the new variational parameter v by using the relation $v^2=\frac{4C}{\omega}+\omega^2$, we obtain

$$\ln Z_{s_1} = \ln (2\pi\beta)^{-3/2} + \int_0^C dc \, \frac{\langle S_1 \rangle}{c}$$

$$= -\frac{3}{2}\ln(2\pi\beta) - \int_\omega^v \frac{v\omega}{2} dc \, \frac{3c\beta}{v\omega c} \cdot \left(\coth\frac{v\beta}{2} - \frac{2}{v\beta} \right)$$

$$= -\frac{3}{2}\ln(2\pi\beta) - 3\ln\left(\frac{v}{\omega}\right) - 3\ln\frac{\sinh v\beta/2}{\sinh \omega\beta/2} , \qquad (5.47)$$

under the condition that Z_{s_1} is the partition function of the free electron when C=0, which is given by $(2\pi\beta)^{-3/2}$.

Finally, we can determine the value of the polaron free energy F by minimizing the value of F_{tr}, which can now be evaluated with the use of (5.45), (5.41), (5.44), and (5.47), with respect to the variational parameters v and ω. Therefore, the polaron average energy, which is closely related to the free energy as follows

$$\bar{E} = \frac{\delta \beta F}{\delta \beta} , \qquad (5.48)$$

and the polaron self energy at any arbitary temperature T,

$$E_s = \bar{E} - \frac{3}{2} kT , \qquad (5.49)$$

where the last term is the free electron energy, can be obtained.

The results of the numerical calculations of the polaron average energy and self energy from the expressions (5.48) and (5.49) will be presented in Chapter VII.