Layer 4

In equilibrium you can always assume the system starts and ends in the ground state, that is what makes the standard Green's function machinery work. Out of equilibrium you cannot. Why? The system has history dah! In other words, it is being driven, and there is no single state it returns to. The time contour has to be modified to handle this.

Step 1 – The Keldysh contour (SPT p.45-46)

Instead of letting time run from $-\infty$ to $+\infty$ once, you run it from $-\infty$ forward to $+\infty$ along the upper half of the complex plane and then back from $+\infty$ to $-\infty$ along the lower half. The key point here is: since the contour ends where it began, you never need to know the final state. The system is forced to return to its starting point by construction.

All propagators defined on this contour are called: contour-ordered propagators. The Green's function is still defined the same way as layer 1: $G = -i\langle T_c \varphi \varphi^+ \rangle$ but where T_c orders along the contour.

Step 2 – $G^{K,R}$ as the physical components

Once we have the contour, we extract the physics by asking where the two time arguments t and t' sit relative to each other.

In the SPT book eq. (3.2):

$$G(x,x') = G^{>}(x,x') \text{ for } t>t' = (-i)\langle \psi(x)\,\psi^{\dagger}(x')\rangle$$

$$G(x,x') = G^{<}(x,x') \text{ for } t<t' = (\mp i)\langle \psi^{\dagger}(x')\,\psi(x)\rangle$$

These are the same $G^{(1)}$ from §1.9 eq. (9.10).

Step 3 – The Langreth rules (SPT eq. 3.7–3.9)

I suppose this is the technical ❤ of the Keldysh formalism. We need rules for projecting the contour ordered result onto real time components of $G^{<}$ and G^{r}.

Result eq. (3.8) is the Langreth rule:

$$A^{<}(t,t') = \int \left[B^{r}(t,\tau)\,C^{<}(\tau,t') + B^{<}(t,\tau)\,C^{a}(\tau,t')\right] d\tau$$

In frequency space this becomes eq. (3.9):

$A^{<}(\omega) = B^{r}(\omega)\,C^{<}(\omega) + B^{<}(\omega)\,C^{a}(\omega)$ and

$A^{r}(\omega) = B^{r}(\omega)\,C^{r}(\omega)$.

The retarded component of a product is the product of retarded components. The lesser are mixes $r, <$ and a in a specific way.

Step 4 – Applying Langreth to the Dyson equation

The Dyson equation is $G = g + g\Sigma G$.

For the retarded component, Langreth gives $G^r = g^r + g^r \Sigma^r G^r$ which rearranges to the same Dyson equation as Layer 3: $G^r = (\omega - H - \Sigma^r)^{-1}$. The retarded component is unchanged by going non-equilibrium. For the lesser component, applying the Langreth rule $A = g + g\Sigma g$ gives (SPT eq. 4.57–4.59, derived step by step):

$G^< = g^r \Sigma^< G^a + \ldots$ after factoring G^a from left and G^r from right this collapses to $G^< = G^r \Sigma^< G^a$.

We call this the Keldysh relation, see eq. (4.59a) in SPT and/or eq. (16) in the model paper. It is the non-equilibrium replacement for the fluctuation-dissipation theorem. Physically, the system occupation $G^<$ is the propagation of whatever the reservoirs inject $\Sigma^<$, modified by the molecular response on both sides.

Step 5 – the lesser self energy $\Sigma^<$ from the reservoirs (SPT eq. 4.60)

What is $\Sigma^<$? Well it is derived in SPT eq. (4.60). Each reservoir contributes $V^<(\omega) = (+1)\, \Sigma_\chi f_\chi(\omega)\, \Gamma_\chi(\omega)$ where $f_\chi(\omega)$ is the Fermi-Dirac function of a reservoir χ and $\Gamma_\chi = -2\,\mathrm{Im}\,\Sigma^r_\chi$ is the coupling strength. In detail:

$\Sigma^<(\omega) = i[\Gamma_L f_L(\omega) + \Gamma_R f_R(\omega)]$. What does this mean?

Well, each reservoir tries to fill states according to its own Fermi function, weighted by how strongly coupled it is. For instance, in equilibrium $\mu_L = \mu_R = \mu$ which means that $f_R = f(\omega) = f_L$ and $\Sigma^< = i\Gamma f(\omega)$ $= 2i f(\omega) \ln \Sigma^r$ which is the fluctuation dissipation theorem from pg 9 §36. Out of equilibrium the two Fermi functions differ, and the molecule sits in competition between them.

Step 6 – the full $G^<$, ¡vamos!

Plugging in $\Sigma^<$ into the Keldysh relation, and expanding order by order in the self energy the model paper says:

$$G^<_{mn} = g^<_m + g^r_m \left[\Sigma^<_{mn} + \Sigma^r_{mn} g^r_n \Sigma^<_{nn} + \Sigma^<_{mn} g^a_n \Sigma^a_{nn} + \dots \right] g^a_n$$

The first term $g^<_m$ is the non interacting baseline, just the Keldysh relation for a single free level. The other terms are corrections from Σ (molecular self energy) which carries spin-orbit coupling and vibrational interactions. The corrections are what generates the non-trivial spin texture $\langle S_m \rangle \neq 0$.