1   Overview

Inhomogeneous systems (liquids in particular) exhibit highly structured density profiles in and outside of equilibrium. These structures and the associated free energy values (the grand potential) can be verified in the near-equilibrium regime. The main assumption here is that the correlations retain their equilibrium functional form. The main tools are various thermodynamic consistency relations, known as "sum rules". For a review of sum rules in charged fluids see [1].

In semiconductor transport
Calibration and verification of these profiles

2   Liquids

2.1   Sum rules

Equilibrium density profiles $\{\rho_0^i(\mathbf{r})\}$ satisfy Euler-Lagrange equations for the grand potential Ω:

$$\frac{\delta\Omega\{\rho_0^i\}}{\delta\rho_i(\mathbf{r})} = 0$$

One sum rule that is easily derivable is:

$$\frac{\partial\Omega}{\partial\mu_i} = \underbrace{\sum_j \int d\mathbf{r}\frac{\delta\Omega}{\delta\rho_i}\frac{\partial\rho_j}{\partial\mu_i}}_{=0} + \frac{\partial}{\partial\mu_i}\sum_j \int d\mathbf{r}\rho_j(\mathbf{r})\left(V_{ext}^j(\mathbf{r}) - \mu_i\right) = -\int d\mathbf{r}\rho_i(\mathbf{r})$$

Gibbs-Duhem sum rule:

$$\frac{\partial p}{\partial\mu_i} = \rho_i$$

Surface tension (verifies energy is computed correctly)

$$\gamma = \frac{1}{A}(\Omega + pV)$$

Gibb's Adsorbtion Theorem (tests both energy and structure calculation, since the left-hand side is computed using energy)

$$\frac{\partial\gamma}{\partial\mu_i} = \frac{1}{A}\left(-int_V d\mathbf{r}\rho_i(\mathbf{r}) + V\rho_i\right) = -\frac{1}{A}\int d\mathbf{r}\left(\rho_i(\mathbf{r}) - \rho_i\right) = T_i$$

Contact Theorem for a planar wall:

$$\sum_i \rho_i^c = \beta p - \sum_i \int dz \rho_i(z) \frac{\partial}{\partial z} \beta V_{ext}^i(z)$$

where z is the transverse coordinate (cite Martin). Curved wall (depends on the curvature, ask Roland for a reference).

Sum rules should not be used to fit parameters but to check consistency of a complete theory (with parameters fixed).

2.2 Checking non-thermodynamically consistent theories (Dirk)

Check the system by computing the solution two different ways (e.g., Picard vs Newton). Check the system piece by piece by adding different components. Mesh convergence. Check against known analytic results (e.g., bulk). Check Newton's method by ensuring quadratic convergence (otherwise, it is indicative of errors in the Jacobian).

3 Semiconductors

Contacts present a problem. The holy grail is to figure out what the physics of contacts is. Metal creates a Shockley barrier at the surface, which is overcome by doping the silicone (heavily) near the contact allowing electrons to tunnel through the Shockley barrier.

3.1 Checks

Particles satisfy Newton's Law.
Add scattering processing one at a time: check known mobility obtained from scattering rates.
Check distribution functions, velocities, generation rates, $I - V$ against the Damocles (the standard for silicone).

Community codes and code repositories (e.g., NanoHUB) become de facto community standards.

Kirkhoff's current law must be checked. In a stationary situation displacement should be zero, and then continuity is checked for the particle current. If the

simulation is done right, particle current through the whole system must account for all types of current. What you see in the local particle motion in TMC contains all of the effects (including the displacement current in the particle velocity), since there is feedback from the particle oscillations.

4   Microscopic consistency

What if thermodynamic time scales cannot be reached, should microscopic consistency be checked. For instance, energy, momentum conservation, Newton's laws.

5   Non-equilibrium checks

By definition: equilibrium means the chemical potential is constant everywhere. Alternatively, all specific particle currents are zero. Ohm's law, Kirkhoff's law. Make sure there is no current w/o external fields (Ohm's law). Deviation from equilibrium in a device (local deviations) must fit known results (intuition).

6   Numerical checks

Distinguish between correct numerics and correct physics. Use mesh convergence to differentiate numeric effects from physical effects. Are travelling plasmon modes near the contacts physical? They go away with a smaller timestep size! However, they have also been physically predicted.

Conservation is a good numerics check.

Particles in a box with elastic collisions: the system will get heated up since momentum is not conserved. Must in principle include coupling to the wall.

References

[1] Ph. A. Martin, *Sum rules in charged fluids*, Rev. Mod. Phys., **60**, 40 (1988).

[2] *A chapter by Jim Henderson in a book edited by Doug Henderson "Theory of inhomogeneous Fluids". "Sum rules in charged fluids"*