S11.A. Beyond the Boltzmann Equation

Read Reichl's narrative on pp.710-1.

For a proper labelling and interpretation of Fig.11.10, read the one-page paper

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Here, we consider the virial expansion of the velocity autocorrelation function.

Consider a classical system of N particles interacting via a central potential. Its Hamiltonian takes the form

$$H^N(\boldsymbol{X}^N) = \sum_{i=1}^{N} \left[\frac{1}{2m} p_i^2 + \sum_{j>i}^{N} V(\,|\,\boldsymbol{q}_i - \boldsymbol{q}_j\,|\,) \right] \qquad \boldsymbol{X}^N = (\boldsymbol{q}^N, \boldsymbol{p}^N) \quad (11.225)$$

The corresponding Liouville operator is [see (6.25-7) of §6.B]

$$\begin{aligned} L^N(\boldsymbol{X}^N) &= -i\{\ ,\ H\}_{\boldsymbol{q},\boldsymbol{p}} \\ &= -i \sum_{k=1}^{N} \left(\frac{\partial H^N}{\partial \boldsymbol{p}_k} \cdot \frac{\partial}{\partial \boldsymbol{q}_k} - \frac{\partial H^N}{\partial \boldsymbol{q}_k} \cdot \frac{\partial}{\partial \boldsymbol{p}_k} \right) \qquad [\, V_{ij} = V(\,|\,\boldsymbol{q}_i - \boldsymbol{q}_j\,|\,)\,] \\ &= -i \sum_{k=1}^{N} \sum_{i=1}^{N} \left[\delta_{ik} \frac{\boldsymbol{p}_i}{m} \cdot \frac{\partial}{\partial \boldsymbol{q}_k} - \sum_{j>i}^{N} \left(\delta_{ik} \frac{\partial V_{ij}}{\partial \boldsymbol{q}_i} + \delta_{jk} \frac{\partial V_{ij}}{\partial \boldsymbol{q}_j} \right) \cdot \frac{\partial}{\partial \boldsymbol{p}_k} \right] \\ &= -i \left[\sum_{k=1}^{N} \frac{\boldsymbol{p}_k}{m} \cdot \frac{\partial}{\partial \boldsymbol{q}_k} - \sum_{k=1}^{N} \sum_{j>k}^{N} \frac{\partial V_{kj}}{\partial \boldsymbol{q}_k} \cdot \frac{\partial}{\partial \boldsymbol{p}_k} - \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{\partial V_{ij}}{\partial \boldsymbol{q}_j} \cdot \frac{\partial}{\partial \boldsymbol{p}_j} \right] \\ &= -i \sum_{k=1}^{N} \left[\frac{\boldsymbol{p}_k}{m} \cdot \frac{\partial}{\partial \boldsymbol{q}_k} - \sum_{j>k}^{N} \frac{\partial V_{kj}}{\partial \boldsymbol{q}_k} \cdot \frac{\partial}{\partial \boldsymbol{p}_k} - \sum_{j>k}^{N} \frac{\partial V_{kj}}{\partial \boldsymbol{q}_j} \cdot \frac{\partial}{\partial \boldsymbol{p}_j} \right] \qquad [\, i \to k \,] \\ &= -i \sum_{k=1}^{N} \left[\frac{\boldsymbol{p}_k}{m} \cdot \frac{\partial}{\partial \boldsymbol{q}_k} - \sum_{j>k}^{N} \frac{\partial V_{kj}}{\partial \boldsymbol{q}_k} \cdot \left(\frac{\partial}{\partial \boldsymbol{p}_k} - \frac{\partial}{\partial \boldsymbol{p}_j} \right) \right] \end{aligned} \quad (11.226)$$

where

$$\frac{\partial V_{kj}}{\partial \boldsymbol{q}_j} = -\frac{\partial V_{kj}}{\partial \boldsymbol{q}_k}$$

The probability density of finding particle 1 at $(\boldsymbol{r}, t)$ is [see (6.31) of §6.B]

$$\begin{aligned} \rho_1(\boldsymbol{r}, t) &= \langle\, \delta[\, \boldsymbol{q}_1(t) - \boldsymbol{r}\,] \,\rangle_\beta \\ &= \int d\boldsymbol{X}^N \rho_{\mathrm{eq}}(\boldsymbol{X}^N)\, \delta[\, \boldsymbol{q}_1(t) - \boldsymbol{r}\,] \\ &= \int d\boldsymbol{X}^N \rho_{\mathrm{eq}}(\boldsymbol{X}^N)\, e^{itL^N} \delta(\, \boldsymbol{q}_1 - \boldsymbol{r}\,) \qquad [\, \boldsymbol{q}_1 = \boldsymbol{q}_1(0)\,] \end{aligned}$$

(11.227)

where

$$\rho_{\mathrm{eq}}(\boldsymbol{X}^N) = \frac{1}{Z} e^{-\beta H^N} \qquad Z = \int d\boldsymbol{X}^N e^{-\beta H^N}$$

(11.228)

The velocity autocorrelation function (or tensor) is defined as

$$\mathbb{C}_{\boldsymbol{v}\boldsymbol{v}}(\boldsymbol{r}, t) = \left\langle\, \boldsymbol{v}(\boldsymbol{0}, 0)\ \boldsymbol{v}^T(\boldsymbol{r}, t) \,\right\rangle_\beta$$

$$= \frac{1}{m^2} \left\langle \boldsymbol{p}_1\, \delta(\boldsymbol{q}_1)\; \boldsymbol{p}_1^T(t)\, \delta[\,\boldsymbol{q}_1(t) - \boldsymbol{r}\,] \right\rangle_\beta \qquad [\, \boldsymbol{p}_1 = \boldsymbol{p}_1(0)\,]$$

$$= \frac{1}{m^2} \int d\boldsymbol{X}^N \rho_{\rm eq}(\boldsymbol{X}^N)\, \boldsymbol{p}_1\, \delta(\boldsymbol{q}_1)\, e^{itL^N} \left[\boldsymbol{p}_1^T\, \delta(\,\boldsymbol{q}_1 - \boldsymbol{r}\,) \right] \qquad (11.229)$$

Its Fourier-Laplace transform is

$$\mathbb{S}_{\boldsymbol{v}\boldsymbol{v}}(\boldsymbol{k}, z) = \int_0^\infty dt\, e^{-zt} \int d\boldsymbol{r}\, e^{-i\boldsymbol{k}\cdot\boldsymbol{r}}\, \mathbb{C}_{\boldsymbol{v}\boldsymbol{v}}(\boldsymbol{r}, t) \qquad (11.230)$$

$$= \int_0^\infty dt\, e^{-zt} \int d\boldsymbol{r}\, e^{-i\boldsymbol{k}\cdot\boldsymbol{r}}\, \frac{1}{m^2} \int d\boldsymbol{X}^N \rho_{\rm eq}(\boldsymbol{X}^N)\, \boldsymbol{p}_1\, \delta(\boldsymbol{q}_1)\, e^{itL^N} \left[\boldsymbol{p}_1^T\, \delta(\,\boldsymbol{q}_1 - \boldsymbol{r}\,) \right]$$

Since L^N is a self-adjoint operator, e^{itL^N} is unitary and we can write (11.230) as [c.f. (6.30) of §6.B]

$$\mathbb{S}_{\boldsymbol{v}\boldsymbol{v}}(\boldsymbol{k}, z) = \int_0^\infty dt\, e^{-zt} \int d\boldsymbol{r}\, e^{-i\boldsymbol{k}\cdot\boldsymbol{r}}\, \frac{1}{m^2} \int d\boldsymbol{X}^N \boldsymbol{p}_1\, \delta(\,\boldsymbol{q}_1 - \boldsymbol{r}\,)\, e^{-itL^N} \left[\rho_{\rm eq}(\boldsymbol{X}^N)\, \delta(\boldsymbol{q}_1)\; \boldsymbol{p}_1^T \right]$$

$$= \frac{1}{m^2} \int_0^\infty dt\, e^{-zt} \int d\boldsymbol{X}^N \boldsymbol{p}_1\, e^{-i\boldsymbol{k}\cdot\boldsymbol{q}_1}\, e^{-itL^N} \left[\rho_{\rm eq}(\boldsymbol{X}^N)\, \delta(\boldsymbol{q}_1)\; \boldsymbol{p}_1^T \right]$$

$$= \frac{1}{m^2} \frac{1}{V} \sum_{\boldsymbol{k}_1} \int_0^\infty dt\, e^{-zt} \int d\boldsymbol{X}^N \boldsymbol{p}_1\, e^{-i\boldsymbol{k}\cdot\boldsymbol{q}_1}\, e^{-itL^N} \left[\rho_{\rm eq}(\boldsymbol{X}^N)\, e^{i\boldsymbol{k}_1\cdot\boldsymbol{q}_1}\; \boldsymbol{p}_1^T \right] \qquad (11.231)$$

$$= \frac{1}{m^2} \int d\boldsymbol{p}_1\, \boldsymbol{p}_1\, \chi(\boldsymbol{p}_1; \boldsymbol{k}, z)\; \boldsymbol{p}_1^T$$

(11.232)

where $\chi(\boldsymbol{p}_1; \boldsymbol{k}, z)$ is a differential operator defined by

$$\chi(\boldsymbol{p}_1; \boldsymbol{k}, z)\, g(\boldsymbol{X}^N) = \frac{1}{V} \sum_{\boldsymbol{k}_1} \int_0^\infty dt\, e^{-zt} \int d\boldsymbol{q}_1 \int d\boldsymbol{X}_2 \ldots \int d\boldsymbol{X}_N$$

$$\times\, e^{-i\boldsymbol{k}\cdot\boldsymbol{q}_1}\, e^{-itL^N} \left[\rho_{\rm eq}(\boldsymbol{X}^N)\, e^{i\boldsymbol{k}_1\cdot\boldsymbol{q}_1}\, g(\boldsymbol{X}^N) \right]$$

(11.233)

for any arbitrary function $g(\boldsymbol{X}^N)$ on the phase space. Note that after the indicated integrations and summations are evaluated, $\chi(\boldsymbol{p}_1; \boldsymbol{k}, z)\, g(\boldsymbol{X}^N)$ is an operator on $\boldsymbol{p}_1$ with parameters $(\boldsymbol{k}, z)$.

If we consider the inter-particle interaction as a perturbation that is turned on adiabatically, we can replace $\rho_{\rm eq}(\boldsymbol{X}^N)$ with the free particle value

$$\rho_{\rm eq}^{(0)}(\boldsymbol{X}^N) = \frac{1}{V^N} \prod_{j=1}^N \phi(j)$$

since $\rho_{\rm eq}(\boldsymbol{X}^N)$ can be taken as the evolution of $\rho_{\rm eq}^{(0)}(\boldsymbol{X}^N)$ from $t = -\infty$ to $t = 0$, i.e.,

$$\rho_{\rm eq}(\boldsymbol{X}^N) = e^{i\infty L^N}\, \rho_{\rm eq}^{(0)}(\boldsymbol{X}^N)$$

In a virial expansion, we set

$$\chi(\boldsymbol{p}_1; \boldsymbol{k}, z) = \sum_{l=0}^\infty n^l\, \chi_l(\boldsymbol{p}_1; \boldsymbol{k}, z) \qquad (11.234)$$

Microscopic expressions for the virial coefficient operators $\chi_l(\boldsymbol{p}_1; \boldsymbol{k}, z)$ can be obtained using a cumulant expansion of the evolution operator [see §4.D.3 & §9.C.1]

$$e^{-itL} = \sum_{N=0}^\infty \frac{1}{N!} e^{-itL^N} = \sum_{N=0}^\infty \frac{1}{N!} S_t(1, \ldots, N) = \exp\left[\sum_{N=1}^\infty \frac{1}{N!} U_t(1, \ldots, N) \right] \qquad (11.235)$$

where $U_t(1, \ldots, N)$ is an *N*-body cluster operator and we have employed the simplified notations $(1, \ldots, N) = (\boldsymbol{X}_1, \ldots, \boldsymbol{X}_N)$. Since relabeling the identical particles does not affect their dynamics, both $S_t(1, \ldots, N)$ and $U_t(1, \ldots, N)$ must be symmetric in their arguments.

Keeping terms involving only up to 4 particles, (11.235) gives

$$\begin{aligned}
&1 + S_t(1) + \frac{1}{2} S_t(1,2) + \frac{1}{3!} S_t(1,2,3) + \frac{1}{4!} S_t(1,2,3,4) + \ldots \\
&= 1 + \left[U_t(1) + \frac{1}{2!} U_t(1,2) + \frac{1}{3!} U_t(1,2,3) + \frac{1}{4!} S_t(1,2,3,4) + \ldots \right] \\
&\quad + \frac{1}{2!} \left[U_t(1) + \frac{1}{2!} U_t(1,2) + \frac{1}{3!} U_t(1,2,3) + \ldots \right]_s^2 \\
&\quad + \frac{1}{3!} \left[U_t(1) + \frac{1}{2!} U_t(1,2) + \ldots \right]_s^3 + \frac{1}{4!} \left[U_t(1) + \ldots \right]_s^4 + \ldots
\end{aligned} \qquad (11.235c)$$

where the subscript s denotes symmetrization of the arguments. For example,

$$\begin{aligned}
&\frac{1}{2} \left[U_t(1) + \frac{1}{2} U_t(1,2) + \frac{1}{3!} U_t(1,2,3) + \ldots \right]_s^2 \\
&= \frac{1}{2} \left[U_t(1)^2 + U_t(1) U_t(1,2) + \frac{1}{3} U_t(1) U_t(1,2,3) + \frac{1}{4} U_t(1,2)^2 + \ldots \right]_s \\
&= \frac{1}{2} U_t(1) U_t(2) + \frac{1}{3!} \left[U_t(1) U_t(2,3) + U_t(2) U_t(1,3) + U_t(3) U_t(1,2) \right] \\
&\quad + \frac{1}{4!} \left[U_t(1) U_t(2,3,4) + U_t(2) U_t(1,3,4) + U_t(3) U_t(1,2,4) + U_t(4) U_t(1,2,3) \right] \\
&\quad + \frac{1}{2 \cdot 4!} \left[U_t(1,2) U_t(3,4) + U_t(1,3) U_t(2,4) + U_t(1,4) U_t(2,3) \right. \\
&\qquad \left. + U_t(2,3) U_t(1,4) + U_t(2,4) U_t(1,3) + U_t(3,4) U_t(1,2) \right] + \ldots
\end{aligned}$$

$$\begin{aligned}
&\frac{1}{3!} \left[U_t(1) + \frac{1}{2} U_t(1,2) + \ldots \right]_s^3 \\
&= \frac{1}{3!} \left[U_t(1)^3 + \frac{3}{2} U_t(1)^2 U_t(1,2) + \ldots \right]_s \\
&= \frac{1}{3!} U_t(1) U_t(2) U_t(3) + \frac{1}{4!} \left[U_t(1) U_t(2) U_t(3,4) + U_t(1) U_t(3) U_t(3,4) + U_t(1) U_t(4) U_t(2,3) \right. \\
&\qquad \left. + U_t(2) U_t(3) U_t(1,4) + U_t(2) U_t(4) U_t(1,3) + U_t(3) U_t(4) U_t(1,2) \right] + \ldots
\end{aligned}$$

Equating each sum of terms involving the same number of particles to zero, (11.235c) gives

$$S_t(1) = U_t(1)$$

(11.236a)

$$S_t(1,2) = U_t(1,2) + U_t(1) U_t(2)$$

(11.236b)

$$\begin{aligned}
S_t(1,2,3) = {} & U_t(1,2,3) + U_t(1) U_t(2,3) + U_t(2) U_t(1,3) + U_t(3) U_t(1,2) \\
& + U_t(1) U_t(2) U_t(3)
\end{aligned}$$

(11.236c)

$$S_t(1,2,3,4) = U_t(1,2,3,4) + U_t(1)\,U_t(2,3,4) + U_t(2)\,U_t(1,3,4)$$
$$+U_t(3)\,U_t(1,2,4) + U_t(4)\,U_t(1,2,3)$$
$$+U_t(1,2)\,U_t(3,4) + U_t(1,3)\,U_t(2,4) + U_t(1,4)\,U_t(2,3)$$
$$+U_t(1)\,U_t(2)\,U_t(3,4) + U_t(1)\,U_t(3)\,U_t(2,4) + U_t(1)\,U_t(4)\,U_t(2,3)$$
$$+U_t(2)\,U_t(3)\,U_t(1,4) + U_t(2)\,U_t(4)\,U_t(1,3) + U_t(3)\,U_t(4)\,U_t(1,2)$$
$$+U_t(1)\,U_t(2)\,U_t(3)\,U_t(4)$$

(11.236d)

$$\vdots$$

which are similar to (9.19-21) of §9.C.1.

Inverting, we get

$$U(1) = S_t(1)$$

(11.236)

$$U(1,2) = S_t(1,2) - U_t(1)\,U_t(2)$$
$$= S_t(1,2) - S_t(1)\,S_t(2)$$

(11.237)

$$U(1,2,3) = S_t(1,2,3) - U_t(1)\,U_t(2,3) - U_t(2)\,U_t(1,3) - U_t(3)\,U_t(1,2) - U_t(1)\,U_t(2)\,U_t(3)$$
$$= S_t(1,2,3) - S_t(1)[\,S_t(2,3) - S_t(2)\,S_t(3)] - S_t(2)[\,S_t(1,3) - S_t(1)\,S_t(3)]$$
$$-S_t(3)[\,S_t(1,2) - S_t(1)\,S_t(2)] - S_t(1)\,S_t(2)\,S_t(3)$$
$$= S_t(1,2,3) - S_t(1)\,S_t(2,3) - S_t(2)\,S_t(1,3) - S_t(3)\,S_t(1,2)$$
$$+2\,S_t(1)\,S_t(2)\,S_t(3)$$

(11.238a)

$$= S_t(1,2,3) - \sum_p^{(3)} S_t(1)\,S_t(2,3) + 2\prod_{i=1}^{3} S_t(i) \qquad (11.238)$$

where

$$\sum_p^{(3)} S_t(1)\,S_t(2,3) = S_t(1)\,S_t(2,3) + S_t(2)\,S_t(1,3) + S_t(3)\,S_t(1,2)$$

with $\sum_p^{(j)}$ indicating a sum over the (j) distinct terms resulted from the permutations of the arguments.

Next, we replace in the R.H.S's of (11.236a-c) all U's that do not involve particle 1 with S's to get

$$S_t(1) = U_t(1) \qquad \text{[Unchanged.]} \qquad (11.239)$$
$$S_t(1,2) = U_t(1)\,S_t(2) + U_t(1,2) \qquad \text{[(11.236) used.]}$$

(11.240)

$$S_t(1,2,3) = U_t(1,2,3) + U_t(1)\left[U_t(2,3) + U_t(2)\,U_t(3)\right] + U_t(2)\,U_t(1,3) + U_t(3)\,U_t(1,2)$$
$$= U_t(1,2,3) + U_t(1)\,S_t(2,3) + S_t(2)\,U_t(1,3) + S_t(3)\,U_t(1,2)$$

(11.241a)

$$= U_t(1)\,S_t(2,3) + \sum_p^{(2)'} U_t(1,2)\,S_t(3) + U_t(1,2,3)$$

(11.241)

where

$$\sum_p^{(2)'} U_t(1, 2)\, S_t(3) = U_t(1, 2)\, S_t(3) + U_t(1, 3)\, S_t(2)$$

with $\sum_p^{(j)'}$ indicating that argument 1 is to be excluded from the permutations so that there are (j) distinct terms in the sum.

$$\begin{aligned} S_t(1, 2, 3, 4) = {} & U_t(1, 2, 3, 4) + U_t(1)\Big[U_t(2, 3, 4) + U_t(2)\, U_t(3, 4) + \\ & U_t(3)\, U_t(2, 4) + U_t(4)\, U_t(2, 3) + U_t(2)\, U_t(3)\, U_t(4)\Big] \\ & + U_t(1, 2)\Big[U_t(3, 4) + U_t(3)\, U_t(4)\Big] \\ & + U_t(1, 3)\Big[U_t(2, 4) + U_t(2)\, U_t(4)\Big] \\ & + U_t(1, 4)\Big[U_t(2, 3) + U_t(2)\, U_t(3)\Big] \\ & + U_t(1, 2, 3)\, U_t(4) + U_t(1, 2, 4)\, U_t(3) + U_t(1, 3, 4)\, U_t(2) \\ = {} & U_t(1, 2, 3, 4) + U_t(1)\, S_t(2, 3, 4) + U_t(1, 2)\, S_t(3, 4) \\ & + U_t(1, 3)\, S_t(2, 4) + U_t(1, 4)\, S_t(2, 3) \\ & + U_t(1, 2, 3)\, S_t(4) + U_t(1, 2, 4)\, S_t(3) + U_t(1, 3, 4)\, S_t(2) \end{aligned}$$

(11.241a)

$$= U_t(1)\, S_t(2, 3, 4) + \sum_p^{(3)'} U_t(1, 2)\, S_t(3, 4) \qquad (11.241b)$$

$$+ \sum_p^{(3)'} U_t(1, 2, 3)\, S_t(4) + U_t(1, 2, 3, 4)$$

Extrapolating to the N-particle case, we have

$$S_t(1, \ldots, N) = U_t(1)\, S_t(2, \ldots, N) + \sum_p^{(N-1)'} U_t(1, 2)\, S_t(3, \ldots, N)$$

$$+ \sum_p^{(N-1)(N-2)/2'} U_t(1, 2, 3)\, S_t(4, \ldots, N) + \ldots + U_t(1, \ldots, N)$$

(11.241c)

where the number of terms in the permutation of the $(2, 3)$ indices in $U_t(1, 2, 3)\, S_t(4, \ldots, N)$ is

$$C_2^{N-1} = \frac{(N-1)!}{(N-3)!\, 2!} = \frac{1}{2}(N-1)(N-2)$$

Since [see (11.235)]

$$e^{-i t L^N} = S_t(1, \ldots, N)$$

substituting (11.241b) into (11.233) gives

$$\chi(\boldsymbol{p}_1; \boldsymbol{k}, z) = \frac{1}{V} \sum_{\boldsymbol{k}_1} \int_0^\infty d\,t\, e^{z\,t} \int d\,\boldsymbol{q}_1 \int d\,\boldsymbol{X}_2 \ldots \int d\,\boldsymbol{X}_N$$
$$\times e^{-i\,\boldsymbol{k}\cdot\boldsymbol{q}_1} \Bigg[U_t(1)\, S_t(2, \ldots, N) + \sum_p^{(N-1)'} U_t(1, 2)\, S_t(3, \ldots, N)$$
$$+ \sum_p^{(N-1)(N-2)/2'} U_t(1, 2, 3)\, S_t(4, \ldots, N) + \ldots + U_t(1, \ldots, N) \Bigg] \rho_{\text{eq}}^{(0)}(\boldsymbol{X}^N)\, e^{i\,\boldsymbol{k}_1\cdot\boldsymbol{q}_1}$$

(11.242)

Now, for $N \geq j \geq 2$

$$\int d\,\boldsymbol{X}_j \ldots \int d\,\boldsymbol{X}_N\, S_t(j, \ldots, N)\, \rho_{\text{eq}}^{(0)}(\boldsymbol{X}^N)$$
$$= \int d\,\boldsymbol{X}_j \ldots \int d\,\boldsymbol{X}_N\, e^{-i\,t\,L^{N-j+1}}\, \rho_{\text{eq}}^{(0)}(\boldsymbol{X}^N)$$
$$= \int d\,\boldsymbol{X}_j \ldots \int d\,\boldsymbol{X}_N\, \rho_{\text{eq}}^{(0)}[\boldsymbol{X}_1, \ldots \boldsymbol{X}_{j-1}, \boldsymbol{X}_j(t), \ldots, \boldsymbol{X}_N(t)]$$
$$= \rho_{\text{eq}}^{(0)}(\boldsymbol{X}_1, \ldots \boldsymbol{X}_{j-1})$$

(11.242a)

Using (11.242a) on (11.242) gives

$$\chi(\boldsymbol{p}_1; \boldsymbol{k}, z) = \frac{1}{V} \sum_{\boldsymbol{k}_1} \int_0^\infty d\,t\, e^{-z\,t} \int d\,\boldsymbol{q}_1\, e^{-i\,\boldsymbol{k}\cdot\boldsymbol{q}_1} \Bigg[U_t(1)\, \rho_{\text{eq}}^{(0)}(1) \qquad (11.244a)$$
$$+ (N-1) \int d\,\boldsymbol{X}_2\, U_t(1, 2)\, \rho_{\text{eq}}^{(0)}(1, 2)$$
$$+ \frac{1}{2}(N-1)(N-2) \int d\,\boldsymbol{X}_2 \int d\,\boldsymbol{X}_3\, U_t(1, 2, 3)\, \rho_{\text{eq}}^{(0)}(1, 2, 3) + \ldots \Bigg] e^{i\,\boldsymbol{k}_1\cdot\boldsymbol{q}_1}$$

where we have made use of the fact that every term in a permutation sum in (11.242) evaluates to the same value.

In the thermodynamic limit,

$$\chi(\boldsymbol{p}_1; \boldsymbol{k}, z) = \int \frac{d\,\boldsymbol{k}_1}{(2\,\pi)^3} \int_0^\infty d\,t\, e^{-z\,t} \int d\,\boldsymbol{q}_1\, e^{-i\,\boldsymbol{k}\cdot\boldsymbol{q}_1} \Bigg[U_t(1)\, \rho_{\text{eq}}^{(0)}(1)$$
$$+ n\,V \int d\,\boldsymbol{X}_2\, U_t(1, 2)\, \rho_{\text{eq}}^{(0)}(1, 2)$$
$$+ \frac{1}{2} n^2\, V^2 \int d\,\boldsymbol{X}_2 \int d\,\boldsymbol{X}_3\, U_t(1, 2, 3)\, \rho_{\text{eq}}(1, 2, 3) + \ldots \Bigg] e^{i\,\boldsymbol{k}_1\cdot\boldsymbol{q}_1}$$

(11.244b)

Note that

$$\rho_{\text{eq}}^{(0)}(1) = \frac{1}{V} \left(\frac{\beta}{2\,\pi\,m} \right)^{3/2} e^{-\beta\,p_1^2/2\,m} \equiv \frac{1}{V}\,\phi(1)$$

(11.243)

$$\rho_{\text{eq}}^{(0)}(1, \ldots, N) = \frac{1}{V^N} \prod_{j=1}^N \phi(j)$$

(11.243a)

Consider now the operator

$$O(\boldsymbol{p}_1) = \int \frac{d\,\boldsymbol{k}_1}{(2\,\pi)^3} \int_0^\infty d\,t\, e^{-z\,t} \int d\,\boldsymbol{q}_1\, e^{-i\,\boldsymbol{k}\cdot\boldsymbol{q}_1}\, U_t(1)\, e^{i\,\boldsymbol{k}_1\cdot\boldsymbol{q}_1}$$

(11.245a)

For an arbitrary function $g(\boldsymbol{p}_1)$,

$$\begin{aligned}
O(\boldsymbol{p}_1)\, g(\boldsymbol{p}_1) &= \int \frac{d\,\boldsymbol{k}_1}{(2\,\pi)^3} \int_0^\infty d\,t\, e^{-z\,t} \int d\,\boldsymbol{q}_1\, e^{-i\,\boldsymbol{k}\cdot\boldsymbol{q}_1}\, U_t(1) \left[e^{i\,\boldsymbol{k}_1\cdot\boldsymbol{q}_1}\, g(\boldsymbol{p}_1) \right] \\
&= \int \frac{d\,\boldsymbol{k}_1}{(2\,\pi)^3} \int_0^\infty d\,t\, e^{-z\,t} \int d\,\boldsymbol{q}_1\, e^{-i\,\boldsymbol{k}\cdot\boldsymbol{q}_1}\, e^{-i\,t\,L^1} \left[e^{i\,\boldsymbol{k}_1\cdot\boldsymbol{q}_1}\, g(\boldsymbol{p}_1) \right] \\
&= \int \frac{d\,\boldsymbol{k}_1}{(2\,\pi)^3} \int d\,\boldsymbol{q}_1\, e^{-i\,\boldsymbol{k}\cdot\boldsymbol{q}_1}\, \frac{1}{z + i\,L^1} \left[e^{i\,\boldsymbol{k}_1\cdot\boldsymbol{q}_1}\, g(\boldsymbol{p}_1) \right] \\
&= \int \frac{d\,\boldsymbol{k}_1}{(2\,\pi)^3} \int d\,\boldsymbol{q}_1\, e^{-i\,\boldsymbol{k}\cdot\boldsymbol{q}_1}\, \frac{1}{z + \frac{\boldsymbol{p}_1}{m}\cdot\frac{\partial}{\partial\,\boldsymbol{q}_1}} \left[e^{i\,\boldsymbol{k}_1\cdot\boldsymbol{q}_1}\, g(\boldsymbol{p}_1) \right] \qquad \text{[(11.226) used.]} \\
&= \int \frac{d\,\boldsymbol{k}_1}{(2\,\pi)^3} \int d\,\boldsymbol{q}_1\, e^{-i\,\boldsymbol{k}\cdot\boldsymbol{q}_1}\, \frac{1}{z + i\,\frac{\boldsymbol{p}_1}{m}\cdot\boldsymbol{k}_1}\, e^{i\,\boldsymbol{k}_1\cdot\boldsymbol{q}_1}\, g(\boldsymbol{p}_1) \\
&= \int d\,\boldsymbol{k}_1\, \delta\,(\boldsymbol{k} - \boldsymbol{k}_1)\, \frac{1}{z + i\,\frac{\boldsymbol{p}_1}{m}\cdot\boldsymbol{k}_1}\, g(\boldsymbol{p}_1) \\
&= \frac{1}{z + i\,\frac{\boldsymbol{p}_1}{m}\cdot\boldsymbol{k}}\, g(\boldsymbol{p}_1)
\end{aligned}$$

(11.245b)

Hence,

$$\int \frac{d\,\boldsymbol{k}_1}{(2\,\pi)^3} \int_0^\infty d\,t\, e^{-z\,t} \int d\,\boldsymbol{q}_1\, e^{-i\,\boldsymbol{k}\cdot\boldsymbol{q}_1}\, U_t(1)\, e^{i\,\boldsymbol{k}_1\cdot\boldsymbol{q}_1} = \frac{1}{z + i\,\frac{\boldsymbol{p}_1}{m}\cdot\boldsymbol{k}} \qquad (11.245)$$

(11.244b) can be written in the form of a virial expansion

$$\chi(\boldsymbol{p}_1;\, \boldsymbol{k},\, z)\, \frac{1}{\phi(1)} = \frac{1}{z + i\,\frac{\boldsymbol{p}_1}{m}\cdot\boldsymbol{k}} + \sum_{l=1}^{\infty} n^l\, \chi_l\,(\boldsymbol{p}_1;\, \boldsymbol{k},\, z)\, \frac{1}{\phi(1)} \qquad (11.246)$$

where

$$\chi_1(\boldsymbol{p}_1;\, \boldsymbol{k},\, z) = \int \frac{d\,\boldsymbol{k}_1}{(2\,\pi)^3} \int_0^\infty d\,t\, e^{-z\,t} \int d\,\boldsymbol{q}_1 \int d\,\boldsymbol{X}_2 \times e^{-i\,\boldsymbol{k}\cdot\boldsymbol{q}_1}\, U_t(1,\, 2) \left[e^{i\,\boldsymbol{k}_1\cdot\boldsymbol{q}_1}\, \phi(1)\, \phi(2) \right] \qquad (11.247)$$

$$\chi_2(\boldsymbol{p}_1;\, \boldsymbol{k},\, z) = \frac{1}{2} \int \frac{d\,\boldsymbol{k}_1}{(2\,\pi)^3} \int_0^\infty d\,t\, e^{-z\,t} \int d\,\boldsymbol{q}_1 \int d\,\boldsymbol{X}_2 \int d\,\boldsymbol{X}_3 \times e^{-i\,\boldsymbol{k}\cdot\boldsymbol{q}_1}\, U_t(1,\, 2,\, 3) \left[e^{i\,\boldsymbol{k}_1\cdot\boldsymbol{q}_1}\, \phi(1)\, \phi(2)\, \phi(3) \right] \qquad (11.248)$$

and so on.

Setting

$$\chi(\boldsymbol{p}_1;\boldsymbol{k},z)\,\frac{1}{\phi(1)} = \frac{1}{z+i\,\frac{\boldsymbol{p}_1}{m}\cdot\boldsymbol{k} - \sum_{l=1}^{\infty} n^l\,B_l(\boldsymbol{p}_1;\boldsymbol{k},z)} \tag{11.249}$$

(11.232) becomes

$$\mathbb{S}_{\boldsymbol{v}\boldsymbol{v}}(\boldsymbol{k},z) = \frac{1}{m^2}\int d\,\boldsymbol{p}_1\,\boldsymbol{p}_1\,\frac{1}{z+i\,\frac{\boldsymbol{p}_1}{m}\cdot\boldsymbol{k} - \sum_{l=1}^{\infty} n^l\,B_l(\boldsymbol{p}_1;\boldsymbol{k},z)}\,\phi(1)\,\boldsymbol{p}_1^T \tag{11.252}$$

(11.249) can be expanded as a power series

$$\begin{aligned}\chi(\boldsymbol{p}_1;\boldsymbol{k},z)\,\frac{1}{\phi(1)} &= \left[1 - \frac{1}{z+i\,\frac{\boldsymbol{p}_1}{m}\cdot\boldsymbol{k}}\sum_{l=1}^{\infty} n^l\,B_l(\boldsymbol{p}_1;\boldsymbol{k},z)\right]^{-1}\frac{1}{z+i\,\frac{\boldsymbol{p}_1}{m}\cdot\boldsymbol{k}}\\ &= \frac{1}{z+i\,\frac{\boldsymbol{p}_1}{m}\cdot\boldsymbol{k}} + \sum_{j=1}^{\infty}\left[\frac{1}{z+i\,\frac{\boldsymbol{p}_1}{m}\cdot\boldsymbol{k}}\sum_{l=1}^{\infty} n^l\,B_l(\boldsymbol{p}_1;\boldsymbol{k},z)\right]^j\frac{1}{z+i\,\frac{\boldsymbol{p}_1}{m}\cdot\boldsymbol{k}}\end{aligned}$$

Comparing with (11.246) then gives

$$\begin{aligned}\sum_{l=1}^{\infty} n^l\,\chi_l(\boldsymbol{p}_1;\boldsymbol{k},z)\,\frac{1}{\phi(1)} &= \sum_{j=1}^{\infty}\left[\frac{1}{z+i\,\frac{\boldsymbol{p}_1}{m}\cdot\boldsymbol{k}}\sum_{l=1}^{\infty} n^l\,B_l(\boldsymbol{p}_1;\boldsymbol{k},z)\right]^j\frac{1}{z+i\,\frac{\boldsymbol{p}_1}{m}\cdot\boldsymbol{k}}\\ &= \frac{1}{z+i\,\frac{\boldsymbol{p}_1}{m}\cdot\boldsymbol{k}}\,n\,B_1(\boldsymbol{p}_1;\boldsymbol{k},z)\,\frac{1}{z+i\,\frac{\boldsymbol{p}_1}{m}\cdot\boldsymbol{k}} + \frac{1}{z+i\,\frac{\boldsymbol{p}_1}{m}\cdot\boldsymbol{k}}\,n^2\,B_2(\boldsymbol{p}_1;\boldsymbol{k},z)\,\frac{1}{z+i\,\frac{\boldsymbol{p}_1}{m}\cdot\boldsymbol{k}} + \ldots\\ &\quad + n^2\,\frac{1}{z+i\,\frac{\boldsymbol{p}_1}{m}\cdot\boldsymbol{k}}\,B_1(\boldsymbol{p}_1;\boldsymbol{k},z)\,\frac{1}{z+i\,\frac{\boldsymbol{p}_1}{m}\cdot\boldsymbol{k}}\,B_1(\boldsymbol{p}_1;\boldsymbol{k},z)\,\frac{1}{z+i\,\frac{\boldsymbol{p}_1}{m}\cdot\boldsymbol{k}} + \ldots\end{aligned}$$

Equating coefficients of each power of n to zero gives

$$\chi_1(\boldsymbol{p}_1;\boldsymbol{k},z)\,\frac{1}{\phi(1)} = \frac{1}{z+i\,\frac{\boldsymbol{p}_1}{m}\cdot\boldsymbol{k}}\,B_1(\boldsymbol{p}_1;\boldsymbol{k},z)\,\frac{1}{z+i\,\frac{\boldsymbol{p}_1}{m}\cdot\boldsymbol{k}} \tag{11.250a}$$

$$\begin{aligned}\chi_2(\boldsymbol{p}_1;\boldsymbol{k},z)\,\frac{1}{\phi(1)} &= \frac{1}{z+i\,\frac{\boldsymbol{p}_1}{m}\cdot\boldsymbol{k}}\,B_2(\boldsymbol{p}_1;\boldsymbol{k},z)\,\frac{1}{z+i\,\frac{\boldsymbol{p}_1}{m}\cdot\boldsymbol{k}}\\ &\quad + \frac{1}{z+i\,\frac{\boldsymbol{p}_1}{m}\cdot\boldsymbol{k}}\,B_1(\boldsymbol{p}_1;\boldsymbol{k},z)\,\frac{1}{z+i\,\frac{\boldsymbol{p}_1}{m}\cdot\boldsymbol{k}}\,B_1(\boldsymbol{p}_1;\boldsymbol{k},z)\,\frac{1}{z+i\,\frac{\boldsymbol{p}_1}{m}\cdot\boldsymbol{k}}\end{aligned} \tag{11.250b}$$

Reminder: χ_l & B_l are differential operators of $\boldsymbol{p}_1$ that act on everything to their right.

Inverting (11.250a), we get

$$B_1(\boldsymbol{p}_1;\boldsymbol{k},z) = \left(z+i\,\frac{\boldsymbol{p}_1}{m}\cdot\boldsymbol{k}\right)\chi_1(\boldsymbol{p}_1;\boldsymbol{k},z)\,\frac{1}{\phi(1)}\left(z+i\,\frac{\boldsymbol{p}_1}{m}\cdot\boldsymbol{k}\right) \tag{11.250}$$

(11.250b) then becomes

$$\chi_2(\boldsymbol{p}_1;\boldsymbol{k},z)\frac{1}{\phi(1)}=\frac{1}{z+i\frac{\boldsymbol{p}_1}{m}\cdot\boldsymbol{k}}B_2(\boldsymbol{p}_1;\boldsymbol{k},z)\frac{1}{z+i\frac{\boldsymbol{p}_1}{m}\cdot\boldsymbol{k}}$$
$$+\chi_1(\boldsymbol{p}_1;\boldsymbol{k},z)\frac{1}{\phi(1)}\left(z+i\frac{\boldsymbol{p}_1}{m}\cdot\boldsymbol{k}\right)\chi_1(\boldsymbol{p}_1;\boldsymbol{k},z)\frac{1}{\phi(1)}$$

Inverting gives

$$B_2(\boldsymbol{p}_1;\boldsymbol{k},z)=\left(z+i\frac{\boldsymbol{p}_1}{m}\cdot\boldsymbol{k}\right)\chi_2(\boldsymbol{p}_1;\boldsymbol{k},z)\frac{1}{\phi(1)}\left(z+i\frac{\boldsymbol{p}_1}{m}\cdot\boldsymbol{k}\right) \tag{11.251}$$
$$-\left(z+i\frac{\boldsymbol{p}_1}{m}\cdot\boldsymbol{k}\right)\chi_1(\boldsymbol{p}_1;\boldsymbol{k},z)\frac{1}{\phi(1)}\left(z+i\frac{\boldsymbol{p}_1}{m}\cdot\boldsymbol{k}\right)\chi_1(\boldsymbol{p}_1;\boldsymbol{k},z)\frac{1}{\phi(1)}\left(z+i\frac{\boldsymbol{p}_1}{m}\cdot\boldsymbol{k}\right)$$

Read pp.716-7 of Reichl’s text.