1　はじめに

Lutsko によるストレスゆらぎと弾性定数の関係式の導出を示す [1]。Lutsko 以前に、Ray らによる導出がある。Ray らの導出ではハミルトニアンに圧力制御のピストンの運動エネルギー、及び、ポテンシャルが現れる。一方、これらは Lusko の導出には現れない。Lusko の導出のほうがわかりやすいためこちらに従う。

2　定義と関係式

系のハミルトニアンは粒子の運動エネルギーとポテンシャルの和で表される。

$$\mathcal{H} = \sum_i \frac{p_i^2}{2m_i} + V(\{\boldsymbol{q}_i\}) \tag{1}$$

ここで、i 番目の粒子の位置 $\boldsymbol{q}_i$、及び、運動量 $\boldsymbol{p}_i$ はそれぞれ 3 次元の縦ベクトルとする。

$$\boldsymbol{q} = \begin{pmatrix} q_1 \\ q_2 \\ q_3 \end{pmatrix}, \quad \boldsymbol{p} = \begin{pmatrix} p_1 \\ p_2 \\ p_3 \end{pmatrix} \tag{2}$$

格子ベクトル $\boldsymbol{a}_1$、$\boldsymbol{a}_2$、$\boldsymbol{a}_3$ を用いて格子行列 H を定義する。

$$\mathrm{H} = \begin{pmatrix} \boldsymbol{a}_1 & \boldsymbol{a}_2 & \boldsymbol{a}_3 \end{pmatrix} = \begin{pmatrix} a_{11} & a_{21} & a_{31} \\ a_{12} & a_{22} & a_{32} \\ a_{13} & a_{23} & a_{33} \end{pmatrix} \tag{3}$$

これらを用いて、内部座標 $\boldsymbol{s}$、及び、スケールされた運動量 $\tilde{p}$ を定義する。

$$\boldsymbol{s} = \mathrm{H}^{-1}\boldsymbol{q}, \quad \tilde{\boldsymbol{p}} = \mathrm{H}^T\boldsymbol{p} \tag{4}$$

$$\begin{aligned} \boldsymbol{q} &= \mathrm{H}\boldsymbol{s} && (5) \\ &= \sum_i s_i \boldsymbol{a}_i && (6) \\ &= \begin{pmatrix} a_{11} & a_{21} & a_{31} \\ a_{12} & a_{22} & a_{32} \\ a_{13} & a_{23} & a_{33} \end{pmatrix} \begin{pmatrix} s_1 \\ s_2 \\ s_3 \end{pmatrix} && (7) \\ \boldsymbol{p} &= (\mathrm{H}^{-1})^T \tilde{\boldsymbol{p}} && (8) \end{aligned}$$

以下では、表記を簡単にするために逆行列の転置を $\mathrm{H}^{-T} := \left(\mathrm{H}^{-1}\right)^T = \left(\mathrm{H}^T\right)^{-1}$ と表す。基準となる平衡状態の格子ベクトルを H_0 として、応力により変形した格子ベクトルを $\mathrm{H} = \mathrm{H}_0 + \delta\mathrm{H}$ とする。

これらを用いて歪みテンソル e を定義し、格子の変形を表す。

$$
\begin{aligned}
\mathrm{H} &= \mathrm{H}_0 + \delta\mathrm{H} && (9)\\
\mathrm{H}^{\mathrm{T}}\mathrm{H} &= (\mathrm{H}_0 + \delta\mathrm{H})^{\mathrm{T}}(\mathrm{H}_0 + \delta\mathrm{H}) && (10)\\
&= \mathrm{H}_0^{\mathrm{T}}\mathrm{H}_0 + \delta\mathrm{H}^{\mathrm{T}}\mathrm{H}_0 + \mathrm{H}_0^{\mathrm{T}}\delta\mathrm{H} + \delta\mathrm{H}^{\mathrm{T}}\delta\mathrm{H} && (11)\\
&\approx \mathrm{H}_0^{\mathrm{T}}\mathrm{H}_0 + \delta\mathrm{H}^{\mathrm{T}}\mathrm{H}_0 + \mathrm{H}_0^{\mathrm{T}}\delta\mathrm{H} && (12)\\
&:= \mathrm{H}_0^{\mathrm{T}}\mathrm{H}_0 + 2\mathrm{H}_0^{\mathrm{T}}\mathrm{e}\mathrm{H}_0 && (13)\\
&= \mathrm{H}_0^{\mathrm{T}}(1 + 2\mathrm{e})\mathrm{H}_0 && (14)\\
\mathrm{e} &:= \frac{1}{2}\left((\mathrm{H}_0^{\mathrm{T}})^{-1}\mathrm{H}^{\mathrm{T}}\mathrm{H}\mathrm{H}_0^{-1} - 1\right) && (15)\\
& && (16)
\end{aligned}
$$

巨視的なストレステンソル $t_{\alpha\beta}$、及び、弾性定数 $C_{\alpha\beta\gamma\sigma}$ はそれぞれヘルムホルツ自由エネルギー F、及び、ストレステンソル $t_{\alpha\beta}$ の歪み e に対する微分として定義される。

$$
t_{\alpha\beta} = -\frac{\partial F}{\partial e_{\alpha\beta}}, \quad C_{\alpha\beta\gamma\sigma} = -\frac{\partial t_{\alpha\beta}}{e_{\gamma\beta}} \tag{17}
$$

弾性定数 $C_{\alpha\beta\gamma\sigma}$ をストレスゆらぎで表すには、これらの微分の表式を求めれば良い。

3　微分の表式

任意のスカラー関数 $A(\{\boldsymbol{q}_i, \boldsymbol{p}_i\})$ の H、e についての微分の表式を求める。まず、変数 $\boldsymbol{q}_i$、$\boldsymbol{p}_i$ の微分を求める。

$$
\begin{aligned}
\frac{\partial q_{i\alpha}}{\partial H_{\beta\gamma}} &= \frac{\partial}{\partial H_{\beta\gamma}}\sum_{\sigma} H_{\alpha\sigma}\mathrm{s}_{\sigma} && (18)\\
&= \sum_{\sigma}\delta_{\alpha\beta}\delta_{\sigma\gamma}s_{\sigma} && (19)\\
&= \delta_{\alpha\beta}s_{\gamma} && (20)\\
&= \delta_{\alpha\beta}(\mathrm{H}^{-1}\boldsymbol{q})_{\gamma} && (21)\\
&= \delta_{\alpha\beta}\sum_{\sigma}\mathrm{H}^{-1}_{\gamma\sigma}\boldsymbol{q}_{\sigma} && (22)
\end{aligned}
$$

$$\frac{\partial \tilde{p}_{i\alpha}}{\partial H_{\beta\gamma}} = \frac{\partial}{\partial H_{\beta\gamma}} \left(\mathrm{H}^T \mathbf{p_i}\right)_\alpha \tag{23}$$

$$0 = \frac{\partial}{\partial H_{\beta\gamma}} \sum_\sigma H^T_{\alpha\sigma} p_{i\sigma} \tag{24}$$

$$= \sum_\sigma \left(\frac{\partial H_{\sigma\alpha}}{\partial H_{\beta\gamma}} p_{i\sigma} + H_{\sigma\alpha} \frac{\partial p_{i\sigma}}{\partial H_{\beta\gamma}}\right) \tag{25}$$

$$= \sum_\sigma \left(\delta_{\sigma\beta}\delta_{\alpha\gamma} p_{i\sigma} + H_{\sigma\alpha} \frac{\partial p_{i\sigma}}{\partial H_{\beta\gamma}}\right) \tag{26}$$

$$= \delta_{\alpha\gamma} p_{i\beta} + \sum_\sigma H_{\sigma\alpha} \frac{\partial p_{i\sigma}}{\partial H_{\beta\gamma}} \tag{27}$$

$$\sum_\sigma H_{\sigma\alpha} \frac{\partial p_{i\sigma}}{\partial H_{\beta\gamma}} = -\delta_{\alpha\gamma} p_{i\beta} \tag{28}$$

$$\sum_\alpha H^{-1}_{\alpha\tau} \sum_\sigma H_{\sigma\alpha} \frac{\partial p_{i\sigma}}{\partial H_{\beta\gamma}} = -\sum_\alpha H^{-1}_{\alpha\tau} \delta_{\alpha\gamma} p_{i\beta} \tag{29}$$

$$\sum_\sigma \left(HH^{-1}\right)_{\sigma\tau} \frac{\partial p_{i\sigma}}{\partial H_{\beta\gamma}} = -H^{-1}_{\gamma\tau} p_{i\beta} \tag{30}$$

$$\sum_\sigma \delta_{\sigma\tau} \frac{\partial p_{i\sigma}}{\partial H_{\beta\gamma}} = -H^{-1}_{\gamma\tau} p_{i\beta} \tag{31}$$

$$\frac{\partial p_{i\tau}}{\partial H_{\beta\gamma}} = -H^{-1}_{\gamma\tau} p_{i\beta} \tag{32}$$

したがって、$q_{i\alpha}$、$p_{i\alpha}$ の $H_{\beta\gamma}$ 微分は以下である。

$$\frac{\partial q_{i\alpha}}{\partial H_{\beta\gamma}} = \delta_{\alpha\beta} \sum_\sigma \mathrm{H}^{-1}_{\gamma\sigma} \boldsymbol{q}_\sigma, \quad \frac{\partial p_{i\alpha}}{\partial H_{\beta\gamma}} = -H^{-1}_{\gamma\alpha} p_{i\beta} \tag{33}$$

スカラー関数 $A\left(\{\boldsymbol{q}_i, \boldsymbol{p}_i\}\right)$ の $H_{\beta\gamma}$ 微分は以下となる。

$$\frac{\partial \mathrm{A}(\{\boldsymbol{q}_i, \boldsymbol{p}_i\})}{\partial H_{\beta\gamma}} = \sum_{i,\alpha} \left\{\frac{\partial \mathrm{A}(\{\boldsymbol{q}_i, \boldsymbol{p}_i\})}{\partial q_{i\alpha}} \frac{\partial q_{i\alpha}}{\partial H_{\beta\gamma}} + \frac{\partial \mathrm{A}(\{\boldsymbol{q}_i, \boldsymbol{p}_i\})}{\partial p_{i\alpha}} \frac{\partial p_{i\alpha}}{\partial H_{\beta\gamma}}\right\} \tag{34}$$

$$= \sum_i \left\{\sum_\alpha \frac{\partial \mathrm{A}(\{\boldsymbol{q}_i, \boldsymbol{p}_i\})}{\partial q_{i\alpha}} \left(\delta_{\alpha\beta} \sum_\sigma \mathrm{H}^{-1}_{\gamma\sigma} q_{i\sigma}\right) + \sum_\alpha \frac{\partial \mathrm{A}(\{\boldsymbol{q}_i, \boldsymbol{p}_i\})}{\partial p_{i\alpha}} \left(-H^{-1}_{\gamma\alpha} p_{i\beta}\right)\right\} \tag{35}$$

$$= \sum_i \left\{\frac{\partial \mathrm{A}(\{\boldsymbol{q}_i, \boldsymbol{p}_i\})}{\partial q_{i\beta}} \sum_\sigma \mathrm{H}^{-1}_{\gamma\sigma} q_{i\sigma} - p_{i\beta} \sum_\alpha H^{-1}_{\gamma\alpha} \frac{\partial \mathrm{A}(\{\boldsymbol{q}_i, \boldsymbol{p}_i\})}{\partial p_{i\alpha}}\right\} \tag{36}$$

$$= \sum_i \left\{\frac{\partial \mathrm{A}(\{\boldsymbol{q}_i, \boldsymbol{p}_i\})}{\partial q_{i\beta}} \left(\mathrm{H}^{-1} q_i\right)_\gamma - p_{i\beta} \left(H^{-1} \frac{\partial \mathrm{A}(\{\boldsymbol{q}_i, \boldsymbol{p}_i\})}{\partial \boldsymbol{p}_i}\right)_\gamma\right\} \tag{37}$$

H の各成分での微分を行列として表すと次式となる。

$$\frac{\partial A}{\partial \mathrm{H}} = \sum_i \left\{\frac{\partial A}{\partial \boldsymbol{q}_i} \otimes \left(\mathrm{H}^{-1} \boldsymbol{q}_i\right) - \boldsymbol{p}_i \otimes \left(\mathrm{H}^{-1} \frac{\partial A}{\partial \boldsymbol{p}_i}\right)\right\} \tag{38}$$

ここで、$\otimes$ はテンソル積を表す。例えば $\mathrm{H}_{\alpha\beta}$ 微分の場合、$\otimes$ の左側、右側はそれぞれ α 成分、β 成分をとる。

歪みテンソル e での微分を計算するために、e の微小変化 de に対する H の変化 dH を求める。

$$\mathrm{H^TH} = \mathrm{H_0^T(1+2e)H_0} \tag{39}$$

$$\mathrm{(H+dH)^T(H+dH)} = \mathrm{H_0^T(1+2(e+de))H_0} \tag{40}$$

$$\mathrm{H^TdH + dH^TH + dH^TdH} = \mathrm{2H_0^TdeH_0} \tag{41}$$

$$\mathrm{de} = \frac{1}{2}\mathrm{H_0}^{-T}\mathrm{(dH^TH + H^TdH)H_0^{-1}} \tag{42}$$

ここで、de は対称行列で表され、独立な成分は 6 個である。対称行列で表される歪みテンソル e に対して、反対称テンソル dw を定義する。

$$\mathrm{dw} := \frac{1}{2}\mathrm{H_0}^{-T}\mathrm{(dH^TH - H^TdH)H_0^{-1}} \tag{43}$$

$$\tag{44}$$

dw の独立な成分は 3 個である。したがって、de と dw とから、H と同様に 9 つの独立な変数が得られる。

$$\mathrm{de + dw} = \mathrm{H_0}^{-T}\mathrm{dH^THH_0^{-1}} \tag{45}$$

$$\mathrm{de - dw} = \mathrm{H_0}^{-T}\mathrm{H^TdHH_0^{-1}} \tag{46}$$

$$\mathrm{dH} = \mathrm{H^{-T}H_0^T(de - dw)H_0} \tag{47}$$

$$\mathrm{dH}^{T} = \mathrm{H_0^T(de + dw)H_0H^{-1}} \tag{48}$$

$$\tag{49}$$

A の歪みに対する微分を求める。

$$dA(\boldsymbol{q}_i, \boldsymbol{p}_i) = \sum_{\alpha,\beta} \frac{\partial A}{\partial H_{\alpha\beta}} dH_{\alpha\beta} \tag{50}$$

$$= \sum_{\alpha,\beta} \frac{\partial A}{\partial H_{\alpha\beta}} dH^T_{\beta\alpha} \tag{51}$$

$$= \mathrm{Tr}\left(\frac{\partial A}{\partial \mathrm{H}}\mathrm{dH}^T\right) \tag{52}$$

$$= \mathrm{Tr}\left(\frac{\partial A}{\partial \mathrm{H}}\left(\mathrm{H_0^T(de+dw)H_0H^{-1}}\right)\right) \tag{53}$$

$$= \mathrm{Tr}\left(\mathrm{H_0H^{-1}}\frac{\partial A}{\partial \mathrm{H}}\mathrm{H}_0^T\mathrm{(de+dw)}\right) \tag{54}$$

$$= \sum_{\alpha\beta}\left(\mathrm{H_0H^{-1}}\frac{\partial A}{\partial \mathrm{H}}\mathrm{H}_0^T\right)_{\alpha\beta}\mathrm{(de+dw)}^T_{\alpha\beta} \tag{55}$$

$$= \sum_{\alpha\beta}\left(\mathrm{H_0H^{-1}}\frac{\partial A}{\partial \mathrm{H}}\mathrm{H}_0^T\right)_{\alpha\beta}\mathrm{(de-dw)}_{\alpha\beta} \tag{56}$$

$$\tag{57}$$

$$
\begin{aligned}
dA(\boldsymbol{q}_i, \boldsymbol{p}_i) &= \sum_{\alpha,\beta} \frac{\partial A}{\partial H_{\alpha\beta}} dH_{\alpha\beta} && (58)\\
&= \sum_{\alpha,\beta} \frac{\partial A}{\partial H^T_{\beta\alpha}} dH_{\alpha\beta} && (59)\\
&= \mathrm{Tr}\left(\frac{\partial A}{\partial \mathrm{H}^{\mathrm{T}}} \mathrm{dH}\right) && (60)\\
&= \mathrm{Tr}\left(\frac{\partial A}{\partial \mathrm{H}^{\mathrm{T}}} \left(\mathrm{H}^{-\mathrm{T}} \mathrm{H}_0^{\mathrm{T}} (\mathrm{de} - \mathrm{dw}) \mathrm{H}_0\right)\right) && (61)\\
&= \mathrm{Tr}\left(\mathrm{H}_0 \frac{\partial A}{\partial \mathrm{H}^{\mathrm{T}}} \mathrm{H}^{-T} \mathrm{H}_0^T (\mathrm{de} - \mathrm{dw})\right) && (62)\\
&= \sum_{\alpha\beta} \left(\mathrm{H}_0 \frac{\partial A}{\partial \mathrm{H}^{\mathrm{T}}} \mathrm{H}^{-T} \mathrm{H}_0^T\right)_{\alpha\beta} (\mathrm{de} - \mathrm{dw})_{\beta\alpha} && (63)\\
&= \sum_{\alpha\beta} \left(\mathrm{H}_0 \frac{\partial A}{\partial \mathrm{H}^{\mathrm{T}}} \mathrm{H}^{-T} \mathrm{H}_0^T\right)_{\alpha\beta} (\mathrm{de} + \mathrm{dw})_{\alpha\beta} && (64)\\
& && (65)
\end{aligned}
$$

$$
\mathrm{dA} = \sum_{\alpha\beta} \left(\frac{1}{2} \left(\mathrm{H}_0 \mathrm{H}^{-1} \frac{\partial A}{\partial \mathrm{H}} \mathrm{H}_0^T + \mathrm{H}_0 \frac{\partial A}{\partial \mathrm{H}^{\mathrm{T}}} \mathrm{H}^{-T} \mathrm{H}_0^T\right)_{\alpha\beta} \mathrm{de}_{\alpha\beta} + \frac{1}{2} \left(\mathrm{H}_0 \mathrm{H}^{-1} \frac{\partial A}{\partial \mathrm{H}} \mathrm{H}_0^T - \mathrm{H}_0 \frac{\partial A}{\partial \mathrm{H}^{\mathrm{T}}} \mathrm{H}^{-T} \mathrm{H}_0^T\right)_{\alpha\beta} \mathrm{dw}_{\alpha\beta} \right) \tag{66}
$$

$$
\frac{\partial \mathcal{H}}{\partial q_{i\alpha}} = \frac{\partial}{\partial q_{i\alpha}} \left(\sum_j \sum_\beta \frac{p_{j\beta}^2}{2m_j} + V\left(\{\boldsymbol{q}_j\}\right) \right) = \frac{\partial}{\partial q_{i\alpha}} V\left(\{\boldsymbol{q}_j\}\right) := V_{i\alpha} \tag{67}
$$

$$
\frac{\partial \mathcal{H}}{\partial p_{i\alpha}} = \frac{\partial}{\partial p_{i\alpha}} \left(\sum_j \sum_\beta \frac{p_{j\beta}^2}{2m_j} + V\left(\{\boldsymbol{q}_j\}\right) \right) = \frac{p_{i\alpha}}{m_i} \tag{68}
$$

$$
\frac{\partial \mathcal{H}}{\partial \boldsymbol{q}_i} = \boldsymbol{V}_i, \qquad \frac{\partial \mathcal{H}}{\partial \boldsymbol{p}_i} = \frac{\boldsymbol{p}_i}{m_i} \tag{69}
$$

$$
\begin{aligned}
\frac{\partial \mathcal{H}}{\partial H_{\alpha\beta}} &= \sum_i \left\{ \frac{\partial \mathcal{H}}{\partial q_{i\alpha}} \left(\mathrm{H}^{-1} q_i\right)_\beta - p_{i\alpha} \left(H^{-1} \frac{\partial \mathcal{H}}{\partial \boldsymbol{p}_i}\right)_\beta \right\} && (70)\\
&= \sum_i \left\{ V_{i\alpha} \left(\mathrm{H}^{-1} q_i\right)_\beta - p_{i\alpha} \left(H^{-1} \frac{\boldsymbol{p}_i}{m_i}\right)_\beta \right\} && (71)\\
&= \sum_i \left\{ V_{i\alpha} \left(\mathrm{H}^{-1} q_i\right)_\beta - p_{i\alpha} \left(\frac{\boldsymbol{p}_i}{m_i} H^{-T}\right)_\beta \right\} && (72)\\
\frac{\partial \mathcal{H}}{\partial \mathrm{H}} &= \sum_i \left\{ \boldsymbol{V}_i \otimes \left(\mathrm{H}^{-1} \boldsymbol{q}_i\right) - \boldsymbol{p}_i \otimes \left(H^{-1} \frac{\boldsymbol{p}_i}{m_i}\right) \right\} && (73)
\end{aligned}
$$

$$\frac{\mathrm{dA}}{\mathrm{de}} = \frac{1}{2}\left(\mathrm{H}_0\mathrm{H}^{-1}\frac{\partial A}{\partial \mathrm{H}}\mathrm{H}_0^T + \mathrm{H}_0\frac{\partial A}{\partial \mathrm{H}^{\mathrm{T}}}\mathrm{H}^{-T}\mathrm{H}_0^T\right) \tag{74}$$

$$\frac{\partial A}{\partial e_{\alpha\sigma}} = \frac{1}{2}\sum_i\sum_{\beta\gamma}\left(\left(\mathrm{H}_0\mathrm{H}^{-1}\right)_{\alpha\beta}\left\{\frac{\partial \mathrm{A}}{\partial q_{i\beta}}\left(\mathrm{H}^{-1}q_i\right)_\gamma - p_{i\beta}\left(H^{-1}\frac{\partial \mathrm{A}}{\partial \boldsymbol{p}_i}\right)_\gamma\right\}\mathrm{H}_{0\gamma\sigma}^T\right. \tag{75}$$

$$\left. + \mathrm{H}_{0\alpha\beta}\left\{\left(\mathrm{H}^{-1}q_i\right)_\beta\frac{\partial \mathrm{A}}{\partial q_{i\gamma}} - \left(H^{-1}\frac{\partial \mathrm{A}}{\partial \boldsymbol{p}_i}\right)_\beta p_{i\gamma}\right\}\left(\mathrm{H}^{-T}\mathrm{H}_0^T\right)_{\gamma\sigma}\right) \tag{76}$$

$$\tag{77}$$

$$\frac{\partial \mathrm{A}(\{\boldsymbol{q}_i,\boldsymbol{p}_i\})}{\partial H_{\beta\gamma}} = \sum_i\left\{\frac{\partial \mathrm{A}(\{\boldsymbol{q}_i,\boldsymbol{p}_i\})}{\partial q_{i\beta}}\left(\mathrm{H}^{-1}q_i\right)_\gamma - p_{i\beta}\left(H^{-1}\frac{\partial \mathrm{A}(\{\boldsymbol{q}_i,\boldsymbol{p}_i\})}{\partial \boldsymbol{p}_i}\right)_\gamma\right\} \tag{78}$$

$$\frac{\partial A}{\partial \mathrm{H}} = \sum_i\left\{\frac{\partial A}{\partial \boldsymbol{q}_i}\otimes\left(\mathrm{H}^{-1}\boldsymbol{q}_i\right) - \boldsymbol{p}_i\otimes\left(\mathrm{H}^{-1}\frac{\partial A}{\partial \boldsymbol{p}_i}\right)\right\} \tag{79}$$

$$\frac{\partial A}{\partial \mathrm{H}^T} = \sum_i\left\{\left(\mathrm{H}^{-1}\boldsymbol{q}_i\right)\otimes\frac{\partial A}{\partial \boldsymbol{q}_i} - \left(\mathrm{H}^{-1}\frac{\partial A}{\partial \boldsymbol{p}_i}\right)\otimes\boldsymbol{p}_i\right\} \tag{80}$$

$$(A\,(b\otimes c))_{ik} = \sum_j A_{ij}b_jc_k = (Ab)_ic_k = (bA^T)_ic_k \tag{81}$$

$$= ((Ab)\otimes c)_{ik} \tag{82}$$

$$= \left((bA^T)\otimes c\right)_{ik} \tag{83}$$

$$((a\otimes b)C)_{ik} = \sum_j a_ib_jC_{jk} \tag{84}$$

$$= (a\otimes(bC))_{ik} \tag{85}$$

$$= \left(a\otimes\left(C^Tb\right)\right)_{ik} \tag{86}$$

$$\mathrm{H}^{-1}\frac{\partial A}{\partial \mathrm{H}} + \frac{\partial A}{\partial \mathrm{H}^T}\mathrm{H}^{-T} = \mathrm{H}^{-1}\sum_i\left\{\frac{\partial A}{\partial \boldsymbol{q}_i}\otimes\left(\mathrm{H}^{-1}\boldsymbol{q}_i\right) - \boldsymbol{p}_i\otimes\left(\mathrm{H}^{-1}\frac{\partial A}{\partial \boldsymbol{p}_i}\right)\right\} \tag{87}$$

$$+ \sum_i\left\{\left(\mathrm{H}^{-1}\boldsymbol{q}_i\right)\otimes\frac{\partial A}{\partial \boldsymbol{q}_i} - \left(\mathrm{H}^{-1}\frac{\partial A}{\partial \boldsymbol{p}_i}\right)\otimes\boldsymbol{p}_i\right\}\mathrm{H}^{-T} \tag{88}$$

$$= \sum_i\left\{H^{-1}\frac{\partial A}{\partial \boldsymbol{q}_i}\otimes H^{-1}\boldsymbol{q}_i - H^{-1}\boldsymbol{p}_i\otimes\left(\mathrm{H}^{-1}\frac{\partial A}{\partial \boldsymbol{p}_i}\right)\right. \tag{89}$$

$$\left. + \left(\mathrm{H}^{-1}\boldsymbol{q}_i\right)\otimes\frac{\partial A}{\partial \boldsymbol{q}_i}\mathrm{H}^{-T} - \left(\mathrm{H}^{-1}\frac{\partial A}{\partial \boldsymbol{p}_i}\right)\otimes\boldsymbol{p}_i\mathrm{H}^{-T}\right\} \tag{90}$$

$$= \sum_i\left\{H^{-1}\frac{\partial A}{\partial \boldsymbol{q}_i}\otimes\left(\boldsymbol{q}_iH^{-T}\right) - \left(H^{-1}\boldsymbol{p}_i\right)\otimes\left(\frac{\partial A}{\partial \boldsymbol{p}_i}\mathrm{H}^{-T}\right)\right. \tag{91}$$

$$\left. + \left(\mathrm{H}^{-1}\boldsymbol{q}_i\right)\otimes\frac{\partial A}{\partial \boldsymbol{q}_i}\mathrm{H}^{-T} - \left(\mathrm{H}^{-1}\frac{\partial A}{\partial \boldsymbol{p}_i}\right)\otimes\left(\boldsymbol{p}_i\mathrm{H}^{-T}\right)\right\} \tag{92}$$

$$= \sum_i\mathrm{H}^{-1}\left\{\frac{\partial A}{\partial \boldsymbol{q}_i}\otimes\boldsymbol{q}_i + \boldsymbol{q}_i\otimes\frac{\partial A}{\partial \boldsymbol{q}_i} - \boldsymbol{p}_i\otimes\frac{\partial A}{\partial \boldsymbol{p}_i} - \frac{\partial A}{\partial \boldsymbol{p}_i}\otimes\boldsymbol{p}_i\right\}\mathrm{H}^{-T} \tag{93}$$

$$:= \mathrm{H}^{-1}(\hat{D}A)\mathrm{H}^{-T} \tag{94}$$

$$\frac{1}{Z}\frac{\partial Z}{\partial H_{\alpha\beta}} = -\frac{1}{k_B T}\left\langle\frac{\partial\mathcal{H}}{\partial H_{\alpha\beta}}\right\rangle \tag{95}$$

$$\frac{\partial\langle A\rangle}{\partial H_{\alpha\beta}} = \frac{\partial}{\partial H_{\alpha\beta}}\frac{1}{Z}\int d\boldsymbol{q}d\boldsymbol{p}A\exp(-\mathcal{H}/k_BT) \tag{96}$$

$$= -\frac{1}{Z^2}\frac{\partial Z}{\partial H_{\alpha\beta}}\int d\boldsymbol{q}d\boldsymbol{p}A\exp(-\mathcal{H}/k_BT) + \frac{1}{Z}\int d\boldsymbol{q}d\boldsymbol{p}\frac{\partial A}{\partial H_{\alpha\beta}}\exp(-\mathcal{H}/k_BT) \tag{97}$$

$$+ \frac{1}{Z}\int d\boldsymbol{q}d\boldsymbol{p}A\frac{\partial}{\partial H_{\alpha\beta}}\exp(-\mathcal{H}/k_BT) \tag{98}$$

$$= -\frac{1}{Z}\left(-\frac{1}{k_BT}\right)\left\langle\frac{\partial\mathcal{H}}{\partial H_{\alpha\beta}}\right\rangle\langle A\rangle + \left\langle\frac{\partial A}{\partial H_{\alpha\beta}}\right\rangle - \frac{1}{Z}\frac{1}{k_BT}\left\langle A\frac{\partial\mathcal{H}}{\partial H_{\alpha\beta}}\right\rangle \tag{99}$$

$$= \left\langle\frac{\partial A}{\partial H_{\alpha\beta}}\right\rangle - \frac{1}{k_BT}\left(\left\langle A\frac{\partial\mathcal{H}}{\partial H_{\alpha\beta}}\right\rangle + \left\langle\frac{\partial\mathcal{H}}{\partial H_{\alpha\beta}}\right\rangle\langle A\rangle\right) \tag{100}$$

$$= \left\langle\frac{\partial A}{\partial H_{\alpha\beta}}\right\rangle - \frac{1}{k_BT}\left(\left\langle A\frac{\partial\mathcal{H}}{\partial H_{\alpha\beta}}\right\rangle + \left\langle\frac{\partial\mathcal{H}}{\partial H_{\alpha\beta}}\right\rangle\langle A\rangle\right) \tag{101}$$

$$\frac{\partial\langle A\rangle}{\partial H_{\alpha\beta}} = \left\langle\frac{\partial A}{\partial H_{\alpha\beta}}\right\rangle - \frac{1}{k_BT}\left(\left\langle A\frac{\partial\mathcal{H}}{\partial H_{\alpha\beta}}\right\rangle + \left\langle\frac{\partial\mathcal{H}}{\partial H_{\alpha\beta}}\right\rangle\langle A\rangle\right) \tag{102}$$

$$\frac{\partial\left\langle A\right\rangle}{\partial e_{\alpha\beta}} = \frac{1}{2}\left(\mathrm{H}_0\mathrm{H}^{-1}\frac{\partial\left\langle A\right\rangle}{\partial\mathrm{H}}\mathrm{H}_0^{T} + \mathrm{H}_0\frac{\partial\left\langle A\right\rangle}{\partial\mathrm{H}^{T}}\mathrm{H}^{-\mathrm{T}}\mathrm{H}_0^{\mathrm{T}}\right)_{\alpha\beta} \tag{103}$$

$$= \frac{1}{2}\mathrm{H}_0\left(\mathrm{H}^{-1}\frac{\partial\left\langle A\right\rangle}{\partial\mathrm{H}} + \frac{\partial\left\langle A\right\rangle}{\partial\mathrm{H}^{T}}\mathrm{H}^{-\mathrm{T}}\right)\mathrm{H}_0^{\mathrm{T}} \tag{104}$$

$$= \frac{1}{2}\mathrm{H}_0\left[\mathrm{H}^{-1}\left\{\left\langle\frac{\partial A}{\partial\mathrm{H}}\right\rangle - \frac{1}{k_BT}\left(\left\langle A\frac{\partial\mathcal{H}}{\partial\mathrm{H}}\right\rangle + \left\langle\frac{\partial\mathcal{H}}{\partial\mathrm{H}}\right\rangle\langle A\rangle\right)\right\}\right. \tag{105}$$

$$\left.+\left\{\left\langle\frac{\partial A}{\partial\mathrm{H}^{T}}\right\rangle - \frac{1}{k_BT}\left(\left\langle A\frac{\partial\mathcal{H}}{\partial\mathrm{H}^{T}}\right\rangle + \left\langle\frac{\partial\mathcal{H}}{\partial\mathrm{H}^{T}}\right\rangle\langle A\rangle\right)\right\}\mathrm{H}^{-\mathrm{T}}\right]\mathrm{H}_0^{\mathrm{T}} \tag{106}$$

$$\tag{107}$$

$$F = -k_B T \ln Z \tag{108}$$

$$\Omega\, t_{\alpha\beta} = -\Omega \frac{\partial F}{\partial e_{\alpha\beta}} \tag{109}$$

$$= k_B T Z^{-1} \frac{\partial Z}{\partial e_{\alpha\beta}} \tag{110}$$

$$= \frac{1}{2} k_B T Z^{-1} \left(\mathrm{H}_0 \mathrm{H}^{-1} \frac{\partial Z}{\partial \mathrm{H}} \mathrm{H}_0^T + \mathrm{H}_0 \frac{\partial Z}{\partial \mathrm{H}^T} \mathrm{H}^{-\mathrm{T}} \mathrm{H}_0^{\mathrm{T}} \right)_{\alpha\beta} \tag{111}$$

$$= \frac{1}{2} k_B T \left\{ \mathrm{H}_0 \mathrm{H}^{-1} \left(-\frac{1}{k_B T} \left\langle \frac{\partial \mathcal{H}}{\partial \mathrm{H}} \right\rangle \right) \mathrm{H}_0^T + \mathrm{H}_0 \left(-\frac{1}{k_B T} \left\langle \frac{\partial \mathcal{H}}{\partial \mathrm{H}^T} \right\rangle \right) \mathrm{H}^{-\mathrm{T}} \mathrm{H}_0^{\mathrm{T}} \right\}_{\alpha\beta} \tag{112}$$

$$= -\frac{1}{2} \sum_i \left\{ \mathrm{H}_0 \mathrm{H}^{-1} \left\langle \boldsymbol{V}_i \otimes \left(\mathrm{H}^{-1} \boldsymbol{q}_i\right) - \boldsymbol{p}_i \otimes \left(\mathrm{H}^{-1} \frac{\boldsymbol{p}_i}{m_i} \right) \right\rangle \mathrm{H}_0^T \right. \tag{113}$$

$$\left. + \mathrm{H}_0 \left\langle \left(\mathrm{H}^{-1} \boldsymbol{q}_i\right) \otimes \boldsymbol{V}_i - \left(\mathrm{H}^{-1} \frac{\boldsymbol{p}_i}{m_i} \right) \otimes \boldsymbol{p}_i \right\rangle \mathrm{H}^{-\mathrm{T}} \mathrm{H}_0^{\mathrm{T}} \right\}_{\alpha\beta} \tag{114}$$

$$= -\frac{1}{2} \sum_i \left\{ \mathrm{H}_0 \mathrm{H}^{-1} \left\langle \boldsymbol{q}_i \otimes \boldsymbol{V}_i \right\rangle \mathrm{H}^{-T} \mathrm{H}_0^T - \mathrm{H}_0 \mathrm{H}^{-1} \left\langle \boldsymbol{p}_i \otimes \frac{\boldsymbol{p}_i}{m_i} \right\rangle \mathrm{H}^{-T} \mathrm{H}_0^T \right. \tag{115}$$

$$\left. + \mathrm{H}_0 \mathrm{H}^{-1} \left\langle \boldsymbol{V}_i \otimes \boldsymbol{q}_i \right\rangle \mathrm{H}^{-\mathrm{T}} \mathrm{H}_0^{\mathrm{T}} - \mathrm{H}_0 \mathrm{H}^{-1} \left\langle \frac{\boldsymbol{p}_i}{m_i} \otimes \boldsymbol{p}_i \right\rangle \mathrm{H}^{-\mathrm{T}} \mathrm{H}_0^{\mathrm{T}} \right\}_{\alpha\beta} \tag{116}$$

$$= -\frac{1}{2} \sum_i \mathrm{H}_0 \mathrm{H}^{-1} \left\{ \left\langle \boldsymbol{q}_i \otimes \boldsymbol{V}_i \right\rangle + \left\langle \boldsymbol{V}_i \otimes \boldsymbol{q}_i \right\rangle - \left\langle \boldsymbol{p}_i \otimes \frac{\boldsymbol{p}_i}{m_i} \right\rangle - \left\langle \frac{\boldsymbol{p}_i}{m_i} \otimes \boldsymbol{p}_i \right\rangle \right\} \mathrm{H}^{-\mathrm{T}} \mathrm{H}_0^{\mathrm{T}} \tag{117}$$

$$:= -\frac{1}{2} \left\langle \hat{D}' \mathcal{H} \right\rangle \tag{118}$$

$$:= \Omega \left\langle t_{\alpha\beta} \right\rangle \tag{119}$$

$$\frac{\partial \mathcal{H}}{\partial \mathrm{H}} = \sum_i \left\{ \boldsymbol{V}_i \otimes \left(\mathrm{H}^{-1} \boldsymbol{q}_i\right) - \boldsymbol{p}_i \otimes \left(\mathrm{H}^{-1} \frac{\boldsymbol{p}_i}{m_i} \right) \right\} \tag{120}$$

$$
\begin{aligned}
C_{\alpha\beta\gamma\sigma} &= -\frac{\partial \left\langle t_{\alpha\beta} \right\rangle}{\partial e_{\gamma\sigma}} && (121)\\
&= -\frac{\partial}{\partial e}\left(-\frac{1}{2\Omega}\left\langle \hat{D}'\mathcal{H} \right\rangle\right) && (122)\\
&= -\left\langle \hat{D}'_{\gamma\sigma}\hat{t}_{\alpha\beta} \right\rangle + \frac{2\Omega}{k_BT}\left(\left\langle \hat{t}_{\alpha\beta}\hat{t}_{\gamma\sigma} \right\rangle - \left\langle \hat{t}_{\alpha\beta} \right\rangle \left\langle \hat{t}_{\sigma\gamma} \right\rangle\right) && (123)\\
&= \frac{1}{\Omega}\left\langle \hat{D}'_{\gamma\sigma}\left(\hat{D}'_{\alpha\beta}\mathcal{H}\right) \right\rangle + \frac{2\Omega}{k_BT}\delta\left(\hat{t}_{\alpha\beta}\hat{t}_{\gamma\sigma}\right) && (124)\\
C_{\alpha\beta\gamma\sigma}\Big|_{e=0} &= \frac{2\Omega}{k_BT}\delta_{\hat{t}_{\alpha\beta}\hat{t}_{\gamma\sigma}} + \frac{1}{\Omega}\hat{S}_{\alpha\beta\gamma\sigma}\left\langle \sum_{i,j} q_{i\gamma}V_{j\alpha,i\sigma}q_{j\beta} + \sum_i q_{i\gamma}V_{i\alpha}\delta_{\beta\sigma} + \sum_i \frac{2}{m_i}p_{i\gamma}p_{i\beta}\delta_{\alpha\sigma} \right\rangle && (125)\\
&= \frac{2\Omega}{k_BT}\delta(\hat{t}_{\alpha\beta}\hat{t}_{\gamma\sigma}) + \frac{1}{\Omega}\hat{S}_{\alpha\beta\gamma\sigma}\left\{\sum_i 2\delta_{\alpha\sigma}\delta_{\gamma\beta}k_BT + \left\langle \sum_{ij} q_{i\gamma}V_{j\alpha,i\sigma}q_{j\beta} \right\rangle + \left\langle \sum_i q_{i\gamma}V_{i\alpha}\delta_{\beta\sigma} \right\rangle\right\} && (126)\\
&= \frac{2\Omega}{k_BT}\delta(\hat{t}_{\alpha\beta}\hat{t}_{\gamma\sigma}) + \frac{4Nk_BT}{\Omega}\left(\delta_{\alpha\sigma}\delta_{\beta\gamma} + \delta_{\beta\sigma}\delta_{\alpha\gamma}\right) && (127)\\
&+ \frac{1}{\Omega}\hat{S}_{\alpha\beta}\hat{S}_{\gamma\sigma}\left\{\left\langle \sum_{ij} q_{i\gamma}V_{j\alpha,i\sigma}q_{j\beta} \right\rangle + \left\langle \sum_i q_{i\gamma}V_{i\alpha} \right\rangle \delta_{\beta\sigma}\right\} && (128)\\
& && (129)
\end{aligned}
$$

$$
\begin{aligned}
\left\langle \frac{1}{m_i}p_{i\gamma}p_{i\beta} \right\rangle &= \frac{1}{m_i}\frac{1}{Z}\int d\boldsymbol{q}^{3N}d\boldsymbol{p}^{3N}p_{i\gamma}p_{i\beta}\exp\left(-\frac{1}{k_BT}\left(\sum_j \frac{p_j^2}{2m_j} + V\left(\{\boldsymbol{q_j}\}\right)\right)\right) && (130)\\
&= \delta_{\gamma\beta}\frac{1}{m_i}\frac{\sqrt{\pi}/2(2m_ik_BT)^{3/2}}{\sqrt{\pi}(2m_ik_BT)^{1/2}} && (131)\\
&= \delta_{\gamma\beta}k_BT && (132)
\end{aligned}
$$

4 Appendix

格子行列 H の逆行列は逆格子ベクトルである。

$$\boldsymbol{a}_i \cdot \boldsymbol{b}_j = \sum_\alpha a_{i\alpha} b_{j\alpha} = 2\pi\delta_{ij} \tag{133}$$

$$a_{11}b_{12} + a_{21}b_{22} + a_{31}b_{32} = a_{11}(a_{23}a_{31} - a_{21}a_{33}) + a_{21}(a_{33}a_{11} - a_{31}a_{13}) + a_{31}(a_{13}a_{21} - a_{11}a_{23}) \tag{134}$$

$$= 0 \tag{135}$$

$$a_{11}b_{11} + a_{21}b_{21} + a_{31}b_{31} = \frac{a_{11}(a_{22}a_{33} - a_{23}a_{32}) + a_{21}(a_{32}a_{13} - a_{33}a_{12}) + a_{31}(a_{12}a_{23} - a_{13}a_{22})}{V/2\pi} \tag{136}$$

$$= \frac{a_{11}(a_{22}a_{33} - a_{23}a_{32}) + a_{12}(a_{23}a_{31} - a_{21}a_{33}) + a_{13}(a_{21}a_{32} - a_{22}a_{31})}{V/2\pi} \tag{137}$$

$$= \frac{\mathbf{a_1} \cdot \mathbf{a_2} \times \mathbf{a_3}}{V/2\pi} \tag{138}$$

$$= 2\pi \tag{139}$$

$$\sum_i a_{i\alpha} b_{i\beta} = a_{i\alpha} a_{i\gamma} \times a_{i\alpha} = 2\pi\delta_{\alpha\beta} \tag{140}$$

$$\mathrm{b}_1 = 2\pi \frac{\mathrm{a}_2 \times \mathrm{a}_3}{V} = \frac{2\pi}{V} \begin{pmatrix} a_{22}a_{33} - a_{23}a_{32} \\ a_{23}a_{31} - a_{21}a_{33} \\ a_{21}a_{32} - a_{22}a_{31} \end{pmatrix} \tag{141}$$

$$\mathrm{b}_2 = 2\pi \frac{\mathrm{a}_3 \times \mathrm{a}_1}{V} \tag{142}$$

$$\mathrm{b}_3 = 2\pi \frac{\mathrm{a}_1 \times \mathrm{a}_2}{V} \tag{143}$$

$$\mathrm{H}^{-1} = \frac{1}{2\pi} \begin{pmatrix} \boldsymbol{b}_1^T \\ \boldsymbol{b}_2^T \\ \boldsymbol{b}_3^T \end{pmatrix} = \frac{1}{2\pi} \begin{pmatrix} b_{11} & b_{12} & b_{13} \\ b_{21} & b_{22} & b_{23} \\ b_{31} & b_{32} & b_{33} \end{pmatrix} \tag{144}$$

$$\tag{145}$$

$$\mathrm{H}^{-1}\mathrm{H} = \frac{1}{2\pi} \begin{pmatrix} b_{11} & b_{12} & b_{13} \\ b_{21} & b_{22} & b_{23} \\ b_{31} & b_{32} & b_{33} \end{pmatrix} \begin{pmatrix} a_{11} & a_{21} & a_{31} \\ a_{12} & a_{22} & a_{32} \\ a_{13} & a_{23} & a_{33} \end{pmatrix} \tag{146}$$

$$= \frac{1}{2\pi} \begin{pmatrix} \sum_\alpha b_{1\alpha}a_{1\alpha} & \sum_\alpha b_{1\alpha}a_{2\alpha} & \sum_\alpha b_{1\alpha}a_{3\alpha} \\ \sum_\alpha b_{2\alpha}a_{1\alpha} & \sum_\alpha b_{2\alpha}a_{2\alpha} & \sum_\alpha b_{2\alpha}a_{3\alpha} \\ \sum_\alpha b_{3\alpha}a_{1\alpha} & \sum_\alpha b_{3\alpha}a_{2\alpha} & \sum_\alpha b_{3\alpha}a_{3\alpha} \end{pmatrix} \tag{147}$$

$$= \mathrm{I} \tag{148}$$

参考文献

[1] J F Lutsko. Generalized expressions for the calculation of elastic constants by computer simulation. *Journal of Applied Physics*, Vol. 65, No. 8, pp. 2991–2997, 1989.