3. 约化分布函数

(1) $p^{(1)}(\vec{r}_1)$: Prob density 特定粒子"1"在 $\vec{r}_1$ 而不管其余粒子在何处，也不管 $\vec{r}^N$ 为多少，一定有 $\int p^{(1)}(\vec{r}_1)d\vec{r}_1=1$

已知：$\int P(r^N)d\vec{r}_1 d\vec{r}_2\cdots d\vec{r}_N=1$

$$\Rightarrow p^{(1)}(\vec{r}_1)=\frac{1}{Z_n}\int d\vec{r}_2 d\vec{r}_3\cdots d\vec{r}_N\, e^{-\beta U(\vec{r}_1;\vec{r}_2\vec{r}_3\cdots\vec{r}_N)}$$

$\hat{\vec{r}}_1$ 固定

* 求 $A(r^N)$ 的平均值.

$$\langle A(r^N)\rangle=\frac{1}{Z_n}\int dr^N A(r^N)e^{-\beta U(r^N)}$$

eg: $$\langle\delta(\vec{r}-\vec{r}_1)\rangle=\frac{1}{Z_N}\int dr^N\delta(\vec{r}-\vec{r}_1)e^{-\beta U(r^N)}$$
$$=\frac{1}{Z_N}\int d\vec{r}_2 d\vec{r}_3\cdots d\vec{r}_N\, e^{-\beta(\vec{r};\vec{r}_2\cdots\vec{r}_N)}$$
$$=p^{(1)}(\vec{r})$$

上式是某个特定的粒子在 $\vec{r}_1$ 的概率，可以预见这个 P 是很小的(小)，下面讨论 $\vec{r}$ 处有粒子的概率（单）

(2) Generalized Distribution Function

$$\rho^{(1)}(\vec{r})=N p^{(1)}(\vec{r})=\sum_{i=1}^{N}\langle\delta(\vec{r}-\vec{r}_i)\rangle\longrightarrow\langle\hat{\rho}(\vec{r})\rangle$$

$$\rightarrow\int\rho^{(1)}(\vec{r})d^3\vec{r}=N$$

$$\hat{\rho}(\vec{r})=\sum_{i=1}^{N}\delta(\vec{r}-\vec{r}_i)$$

$\hat{\rho}(\vec{r})$ 依赖于粒子的构型.

若 $\rho^{(1)}(\vec{r})=\text{const}$，即粒子均匀分布

$$\rho^{(1)}(\vec{r})=\langle\hat{\rho}(\vec{r})\rangle$$

(3) $p^{(2)}(\vec{r},\vec{r}')$：有 $\int p^{(2)}(\vec{r},\vec{r}')d\vec{r}d\vec{r}'=1$.

(Specific "1" "2")

$$\Rightarrow p^{(2)}(\vec{r},\vec{r}')=\frac{1}{Z_n}\int d\vec{r}_3 d\vec{r}_4\cdots d\vec{r}_N\, e^{-\beta U(\vec{r},\vec{r}';\vec{r}_3\vec{r}_4\cdots\vec{r}_N)}$$
$$=\frac{1}{Z_n}\int d\vec{r}_{N-2}\int d\vec{r}_1 d\vec{r}_2\,\delta(\vec{r}-\vec{r}_1)\delta(\vec{r}'-\vec{r}_2)e^{-\beta U(\vec{r}_1,\vec{r}_2\cdots\vec{r}_N)}$$
$$=\langle\delta(\vec{r}-\vec{r}_1)\delta(\vec{r}'-\vec{r}_2)\rangle$$

那么$\left\langle \sum_{i=1}^{N}\sum_{j\neq i}^{N}\delta(\vec{r}-\vec{r}_i)\delta(\vec{r}'-\vec{r}_j)\right\rangle = N(N-1)\,\rho^{(\frac{2}{N})}(\vec{r},\vec{r}')$

$$\longrightarrow \rho^{(\frac{2}{N})}(\vec{r},\vec{r}')$$

$$\int \rho^{(\frac{2}{N})}(\vec{r},\vec{r}')\,d\vec{r}\,d\vec{r}' = N(N-1)$$

$\rho^{(\frac{2}{N})}(\vec{r},\vec{r}') \sim \frac{N(N-1)}{V^2} \sim \rho^2$ $\rho^{(\frac{2}{N})}(\vec{r},\vec{r}')$代表$\vec{r},\vec{r}'$的某种关联

定义：$g(\vec{r},\vec{r}') = \dfrac{\rho^{(2)}(\vec{r},\vec{r}')}{\rho^2}$ $\rho^{(2)}(\vec{r},\vec{r}')$即上面的$\rho^{(\frac{2}{N})}(\vec{r},\vec{r}')$

3. 对关联函数

(1) 定义 $g(\vec{r},\vec{r}') = \dfrac{\rho^{(2)}(\vec{r},\vec{r}')}{\rho^2}$ $\rho^{(2)}(\vec{r},\vec{r}') = \dfrac{N(N-1)}{Z_n}\int d\vec{r}_3\ldots d\vec{r}_N e^{-\beta U(\vec{r},\vec{r}';\, r^{N-2})}$

(2) 流体 $\longrightarrow$ 平移不变性. 因此$g(\vec{r},\vec{r}')$应只与相对位置有关

即 $g(\vec{r}_1,\vec{r}_2) = g(\vec{r}_1-\vec{r}_2)$ 记 $\vec{r}=\vec{r}_1-\vec{r}_2$

则 $g = g(\vec{r})$

流体 $\longrightarrow$ 各向同性. 因此 $g(\vec{r}) = g(r)$ $\longrightarrow$ 反映某种径向分布.

(3) 理想气体

$g(\vec{r}_1,\vec{r}_2) = \dfrac{\rho^{(2)}(\vec{r}_1,\vec{r}_2)}{\rho^2}$ $Z_n = \int dr^N e^{-\beta\times 0} = V^N$

则 $\rho^{(2)}(\vec{r}_1,\vec{r}_2) = \dfrac{N(N-1)}{V^2}$ 而 $\rho = \dfrac{N}{V}$

$\Rightarrow$ $g(\vec{r}_1,\vec{r}_2) = \dfrac{N(N-1)}{N^2} \approx 1. = g(r)$ 即$g(r)=1$表示无关联，有时引入$h(r)=g(r)-1$，使无关联时$h(r)=0$.

(4) $\lim\limits_{r\to\infty} g(r) \to 1.$ (无关联)

$\lim\limits_{r\to 0} g(r) \to 0$ ($e^{-\beta U}$中$U\to\infty$)

(5) $\rho^2\int d\vec{r}_1\, d\vec{r}_2\, g(\vec{r}_1-\vec{r}_2) = N(N-1)$

利用平移不变性$\longrightarrow$ $\rho^2\int d\vec{r}_2 \left[\int d\underbrace{(\vec{r}_1-\vec{r}_2)}_{\vec{r}}\, g(\underbrace{\vec{r}_1-\vec{r}_2}_{\vec{r}})\right]$ "[ ]"内的与$\vec{r}_2$无关 $\vec{r}_2$可以积分掉.

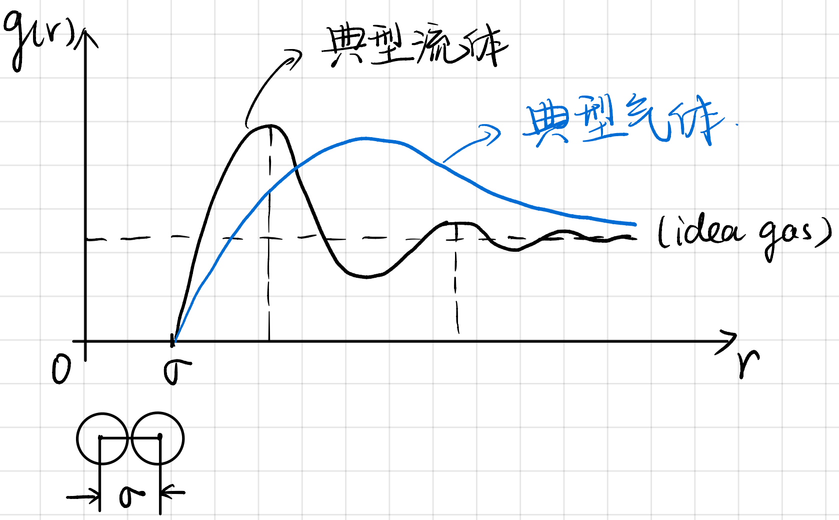
$d\vec{r}_2$积分得V.

$$= N\rho\int d\vec{r}\, g(\vec{r}) \xrightarrow{各向同性} N\int \underbrace{[\rho g(r)]}_{代表径向r处的密度} 4\pi r^2 dr$$

则 $N\int[\rho g(r)]4\pi r^2 dr = N(N-1)$

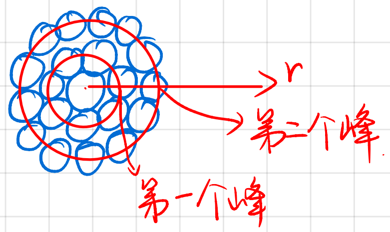
$\Rightarrow \int d\vec{r}\,[\rho g(r)] = N-1$ 给定了一个粒子，因此为$N-1$

$\longrightarrow \int_0^{R_0}(4\pi r^2 dr)[\rho g(r)] \sim R_0$内近邻的粒子数.

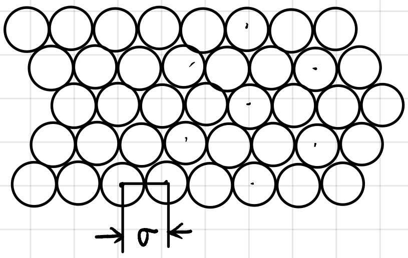


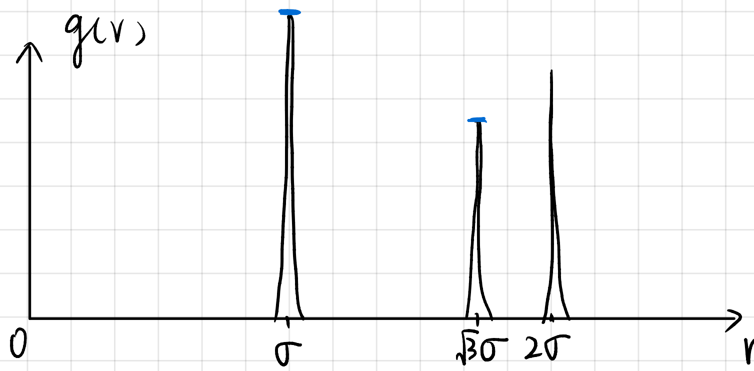
注意峰与谷的位置与流体短程序导致的微观结构有关.

eg:



对固体，我们也可以定义$g(r)$ 下面以二维结构为例





注意到 $\int_0^{\sigma+\varepsilon}4\pi r^2\rho g(r)\,dr$ 为最近邻配位数.

最近邻(σ)与次近邻($\sqrt{3}\sigma$)配位数相同，

但次近邻r大，因此$g(r)$小.

(6) $\langle \sum_{i\neq j} f(\vec{r}_i,\vec{r}_j)\rangle$

$$= \frac{1}{Z_N}\int dr^N e^{-\beta U}\left(\sum_{i\neq j} f(\vec{r}_i,\vec{r}_j)\right)$$

(N(N-1)个)

$$= \frac{N(N-1)}{Z_N}\int dr^N e^{-\beta U} f(\vec{r}_1,\vec{r}_2)$$ (利用 $\langle f(\vec{r}_1,\vec{r}_2)\rangle=\langle f(\vec{r}_2,\vec{r}_3)\rangle=\cdots$)

$$= \int d\vec{r}_1 d\vec{r}_2 f(\vec{r}_1,\vec{r}_2) \times \underbrace{\left[\frac{N(N-1)}{Z_N}\int d\vec{r}_3 \cdots d\vec{r}_N e^{-\beta U}\right]}_{} = \rho^{(2)}(\vec{r}_1,\vec{r}_2)$$

$$= \int d\vec{r}_1 d\vec{r}_2 f(\vec{r}_1,\vec{r}_2)\left[\rho^2 g(\vec{r}_1,\vec{r}_2)\right]$$

$*$ 若 $f(\vec{r}_1,\vec{r}_2) = f(\vec{r}_1-\vec{r}_2)\ (f(\vec{r}))$

$$= N\int d\vec{r}\, f(\vec{r})\left[\rho g(\vec{r})\right] \xrightarrow{\text{各向同性}} N\int 4\pi r^2 dr\, f(r)\left[\rho g(r)\right]$$

eg: $\left\langle \sum_{i\neq j} e^{-i\vec{q}\cdot(\vec{r}_i-\vec{r}_j)} \right\rangle$

$$= N\int d\vec{r}\, e^{-i\vec{q}\cdot\vec{r}}\left[\rho g(\vec{r})\right]$$

$$= N\rho \underbrace{\int d\vec{r}\, e^{-i\vec{q}\cdot\vec{r}} g(\vec{r})}_{}$$

$g(\vec{r})$ 的 Fourier Transform，与 X-Ray 衍射的结构因子有关

§.3. 热力学性质

1. 内能：$E = \langle K\rangle + \langle U\rangle$

之前分析过，$\langle K\rangle$ 与构型无关，$\langle K\rangle = \dfrac{\int e^{-\beta U} K\, d\Gamma}{\int e^{-\beta U} d\Gamma} = \dfrac{3}{2}NkT$

$$\langle U\rangle = \frac{1}{Z_N}\int e^{-\beta U} U\, dr^N$$

$*$ 考察两体势 $U = \frac{1}{2}\sum_{i\neq j} u(\vec{r}_i,\vec{r}_j) = \frac{1}{2}\sum_{i\neq j} u(r_{ij})$

$$\langle U\rangle = \frac{1}{2}\sum_{i\neq j}\langle u(r_{ij})\rangle$$

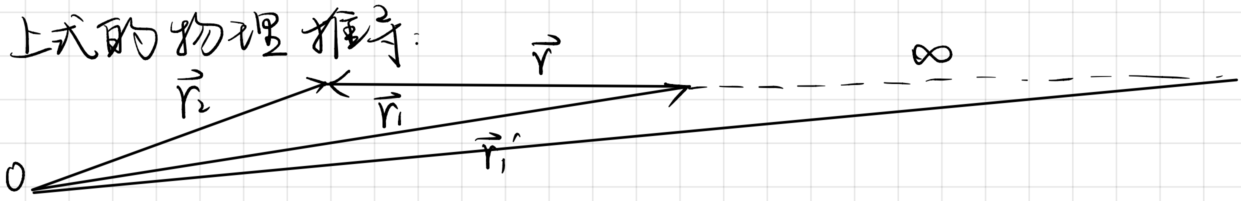
$$= \frac{1}{2}N\int (4\pi r^2 dr)\, u(r)\left[\rho g(r)\right]$$

2. 平均力势 (POF: Potential Of Mean Force)

平衡时 $g(r)$ 的起伏可以等效于某种势 (Potential)，下面我们要将 $g(r)$ 与能量联系在一起

(1) $-k_BT \ln g(r) = W(r)$

(2) 上式的物理推导：



固定$\vec{r}_2$，其余粒子不固定，有涨落，将$\vec{r}_1$从∞远处移到$\vec{r}$处的势能为$W(r)$，此时系统3~N号粒子自由，$\vec{r}_1,\vec{r}_2$固定(constrained ensemble)

$$\vec{F}_1=-\frac{\partial}{\partial \vec{r}_1}U$$

$$\rightarrow \langle \vec{F}_1\rangle_{12}=-\frac{\int d\vec{r}_3\cdots d\vec{r}_N\, e^{-\beta U}\left(\frac{\partial}{\partial \vec{r}_1}U\right)}{\int d\vec{r}_3\cdots d\vec{r}_N\, e^{-\beta U}}$$ 利用 $\frac{\partial}{\partial \vec{r}_1}(e^{-\beta U})=-\beta e^{-\beta U}\frac{\partial}{\partial \vec{r}_1}U$

$$=k_BT\frac{\int d\vec{r}_3\cdots d\vec{r}_N\, \frac{\partial}{\partial \vec{r}_1}(e^{-\beta U})}{\int d\vec{r}_3\cdots d\vec{r}_N\, e^{-\beta U}}$$

$$=k_BT\frac{\partial}{\partial \vec{r}_1}\ln\left(\int dr^{N-2}e^{-\beta U}\right)$$ $\left(\frac{N(N-1)}{Z_n}\int dr^{N-2}e^{-\beta U}=\rho^{(2)}(\vec{r}_1,\vec{r}_2)\right)$ $=\rho^2 g(\vec{r}_1,\vec{r}_2)$

$$=k_BT\frac{\partial}{\partial \vec{r}_1}\ln\left(\rho^2 g(\vec{r}_1,\vec{r}_2)Z_n/N(N-1)\right)$$

$$=k_BT\frac{\partial}{\partial \vec{r}_1}\ln g(\vec{r}_1,\vec{r}_2)$$ (只有$g(\vec{r}_1,\vec{r}_2)$中含$\vec{r}_1$)

$$W(\infty)-W(r)=\int_{\infty}^{\vec{r}_2+\vec{r}}\langle \vec{F}_1\rangle\cdot d\vec{r}_1$$

$$\Rightarrow W(r)=-\int_{\infty}^{\vec{r}_2+\vec{r}}k_BT\left[\frac{\partial}{\partial \vec{r}_1}\ln g(\vec{r}_1,\vec{r}_2)\right]d\vec{r}_1$$

$$=-k_BT\ln g(\vec{r}_1,\vec{r}_2)\Big|_{\vec{r}_1=\vec{r}_2+\infty}^{\vec{r}_1=\vec{r}_2+\vec{r}}$$

$$=k_BT\ln \underbrace{g(\vec{r}_2+\infty,\vec{r}_2)}_{=1}-k_BT\ln \underbrace{g(\vec{r}_2+\vec{r},\vec{r}_2)}_{=g(\vec{r})=g(r)}$$

$$=-k_BT\ln g(r)=W(r)$$

* 稀薄气体 $-k_BT\ln g(r)=u(r)$（无其余粒子的作用）

3. 压强（两体势系统 $U=\frac{1}{2}\sum_{i\neq j}u(r_{ij})$）

(1) 理想气体 $\beta P=\frac{N}{V}=\rho$，但存在相互作用时，$\beta P=\rho+B_2(T)\rho^2+O(\rho^3)$

$B_2(T)$称为第二维里系数，统计力学要找出$B_2(T)$与$u(r)$的关系，

有以下结论：$\beta P=\rho+B_2(T)\rho^2$

$$\rho B_2(T)=-\frac{1}{6k_BT}\int d\vec{r}\left[\rho g(r)\cdot r\frac{du(r)}{dr}\right]$$

证明思路：$P = -\left(\frac{\partial F}{\partial V}\right)_{N,T}$，作业7.11

(2) ρ小，$w(r) \sim u(r)$ $\quad g(r) = e^{-\beta w(r)} \approx e^{-\beta u(r)}$

$$B_2(T) = -\frac{\beta}{6}\int\left\{\left[e^{-\beta u(r)}\frac{du(r)}{dr}\right]r\right\}4\pi r^2 dr$$

$$= \frac{1}{6}\int_0^\infty dr \cdot 4\pi r^3 \frac{d}{dr}\left(e^{-\beta u(r)}+c\right)$$

$$= \underbrace{\frac{2\pi}{3}r^3\left(e^{-\beta u(r)}+c\right)\Big|_{r=0}^{r=\infty}}_{\text{使边界项为0} \Rightarrow c=-1} - \int_0^\infty dr\left(e^{-\beta u(r)}-c\right)\frac{d}{dr}\left(\frac{2}{3}\pi r^3\right)$$

$$\Rightarrow B_2(T) = -\int_0^\infty dr\,(2\pi r^2)\left[e^{-\beta u(r)}-1\right]$$

$$= -\frac{1}{2}\int d\vec{r}\left[e^{-\beta u(r)}-1\right] = -\frac{1}{2}\int d\vec{r}\, f(r)$$

$\left(f(r) = e^{-\beta u(r)}-1\right)$ （作业. 7.12、7.13、7.14）

证明 p 的表达式：

$p = -\left(\frac{\partial F}{\partial V}\right)_{N,T}$ $\quad F = -kT\ln Q_{cl}$ $\quad Q_{cl} = \frac{1}{N!\,\lambda^{3N}}\int d r^N e^{-\beta U(r^N)}$

$$\Rightarrow p = \frac{\partial kT\ln Q}{\partial V}\Big|_{N,T} = \frac{kT}{Z_n}\frac{\partial}{\partial V}Z_n$$

$$\frac{\partial}{\partial V}Z_n = \frac{\partial}{\partial V}\int d\vec{r}_1\cdots d\vec{r}_N\, e^{-\beta U(\vec{r}_1,\cdots\vec{r}_N)}$$

令 $x_i' = \frac{1}{V^{\frac{1}{3}}}x_i$ 则 $Z_n = V^N\underbrace{\int d\vec{r}_i'}_{\text{与V无关}} e^{-\beta U(V^{\frac{1}{3}}\vec{r}_1'\cdots V^{\frac{1}{3}}\vec{r}_N)}$

$$\Rightarrow \frac{\partial}{\partial V}Z_n = \left[\frac{\partial}{\partial V}(V^N)\right]\int d\vec{r}'^N e^{-\beta U(\vec{r}^N)} + V^N\int d\vec{r}'^N\frac{\partial}{\partial V}e^{-\beta U(\vec{r}^N)}$$

$$\frac{N}{V}\int d\vec{r}^N e^{-\beta U(\vec{r}^N)}$$

$$= \rho Z_n$$

$$\frac{\partial}{\partial V}U(\vec{r}^N) = \frac{1}{2}\sum_{i\neq j}\frac{\partial}{\partial V}u(r_{ij})$$

$$= \frac{\partial u(r_{ij})}{\partial r_{ij}}\frac{\partial r_{ij}}{\partial V}$$

而 $r_{ij} \propto V^{\frac{1}{3}} \Rightarrow \frac{dr_{ij}}{dV} = \frac{r_{ij}}{3V}$

则 $\frac{\partial}{\partial V}Z_n$ 中第二项为

$$\int dr^N (-\beta) e^{-\beta U}\left[\frac{1}{2}\sum_{i\neq j}\frac{r_{ij}}{3V}\cdot\frac{\partial u(r_{ij})}{\partial r_{ij}}\right]$$

$$= -\frac{\beta}{6V}\int dr^N e^{-\beta U}\left(\sum_{i\neq j} r_{ij}\frac{\partial u_{ij}}{\partial r_{ij}}\right)$$

$$= -\frac{\beta}{6V}\int dr^N\, N(N-1)\, e^{-\beta U}\, r_{12}\frac{\partial u(r_{12})}{\partial r_{12}}$$

$$= -\frac{\beta}{6V}\int d\vec{r}_1 d\vec{r}_2\, r_{12}\frac{\partial u(r_{12})}{\partial r_{12}}\cdot \underbrace{N(N-1)\int dr^{N-2}e^{-\beta U}} \quad = Z_n\,\rho^2 g(\vec{r}_1,\vec{r}_2)$$

$$= -\frac{\beta}{6V}\int d\vec{r}_1 d\vec{r}_2\, r_{12}\frac{\partial u(r_{12})}{\partial r_{12}}\,\rho^2 g(\vec{r}_1,\vec{r}_2)\cdot Z_n$$

(利用平移不变性 令 $\vec{r}_1-\vec{r}_2=\vec{r}$)

$$= -\frac{\beta}{6V}\underbrace{\int d\vec{r}_2}_{=V}\int d\vec{r}\; r\frac{\partial u(r)}{\partial r}\rho^2 g(\vec{r})\cdot Z_n$$

(利用各向同性, $g(\vec{r})=g(r)$)

$$= -\frac{\beta\rho}{6}\int d\vec{r}\,[\rho g(r)]\, r\frac{\partial u(r)}{\partial r}\cdot Z_n = \rho^2 B_2(T) Z_n$$

代回原式

$$p = k_BT\frac{1}{Z_n}\frac{\partial}{\partial V}Z_n = (\rho + B_2(T)\rho^2)k_BT$$

$$\Rightarrow \beta p = \rho + B_2(T)\rho^2$$

4. 化学势 μ $\quad G = F - TS + pV = \mu N$

对于只与构型有关的物理量 $A(r^N)$ $\quad \langle A\rangle = \int A(r^N)e^{-\beta U(r^N)}/Z_n$

这些量统称为力学量. p 也是此类量.(位力定理告诉我们 $p\propto\sum\langle \vec{F}_i\cdot\vec{r}_i\rangle$)

但对于 S, $S\neq S(r^N)$, 即一个构型没有熵, 而是与所有系综有关, 类似于熵这一类的物理量称为热力学量.

$$dF = -SdT - pdV + \mu dN$$

当 $N\to\infty$ 时 $\quad \frac{\Delta F}{\Delta N} = F_N - F_{N-1}$