PEKING UNIVERSITY

统计力学及应用作业 4

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根据教材的 (15.8) 有

$$S = -\left(\frac{\partial G}{\partial T}\right)_P, \quad V = \left(\frac{\partial G}{\partial P}\right)_T. \tag{1.1}$$

又根据

$$G = E - TS + PV, \tag{1.2}$$

$$G = F + PV, \tag{1.3}$$

$$G = H - TS. \tag{1.4}$$

得

$$E = G - T\left(\frac{\partial G}{\partial T}\right)_P + P\left(\frac{\partial G}{\partial P}\right)_T, \tag{1.5}$$

$$F = G - P\left(\frac{\partial G}{\partial P}\right)_T, \tag{1.6}$$

$$H = G - T\left(\frac{\partial G}{\partial T}\right)_P. \tag{1.7}$$

又

$$C_p = \left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial\left(G - T\left(\frac{\partial G}{\partial T}\right)_P\right)}{\partial T}\right)_P. \tag{1.8}$$

$$C_v = C_p + T\frac{\left(\frac{\partial V}{\partial T}\right)_P^2}{\left(\frac{\partial V}{\partial P}\right)_T} = \left(\frac{\partial\left(G - T\left(\frac{\partial G}{\partial T}\right)_P\right)}{\partial T}\right)_P + T\frac{\left(\frac{\partial\left(\frac{\partial G}{\partial P}\right)_T}{\partial T}\right)_P^2}{\left(\frac{\partial\left(\frac{\partial G}{\partial P}\right)_T}{\partial P}\right)_T}. \tag{1.9}$$

$\square$

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$$C_p = T\left(\frac{\partial S}{\partial T}\right)_P = T\frac{\partial(S,P)}{\partial(T,P)} = T\frac{\partial(S,P)/\partial(T,V)}{\partial(T,P)/\partial(T,V)} \tag{2.1}$$

$$= T\frac{\left(\frac{\partial S}{\partial T}\right)_V\left(\frac{\partial P}{\partial V}\right)_T - \left(\frac{\partial S}{\partial V}\right)_T\left(\frac{\partial P}{\partial T}\right)_V}{\left(\frac{\partial P}{\partial V}\right)_T} \tag{2.2}$$

$$= C_v - T\frac{\left(\frac{\partial S}{\partial V}\right)_T\left(\frac{\partial P}{\partial T}\right)_V}{\left(\frac{\partial P}{\partial V}\right)_T} \tag{2.3}$$

$$= C_v - T\frac{\left(\frac{\partial P}{\partial T}\right)_V^2}{\left(\frac{\partial P}{\partial V}\right)_T}, \tag{2.4}$$

即

$$C_p - C_v = -T\frac{\left(\frac{\partial P}{\partial T}\right)_V^2}{\left(\frac{\partial P}{\partial V}\right)_T}. \quad \square \tag{2.5}$$

3

1

不能, 只能通过状态方程求出 C_p, C_v 的差.

2

通过测量 C_p 或 C_v, 然后积分

$$C_v = T\left(\frac{\partial S}{\partial T}\right)_V \tag{3.1}$$

得 S, 然后通过积分

$$\mathrm{d}E = T\,\mathrm{d}S - P\,\mathrm{d}V, \tag{3.2}$$

得 E, 然后可得

$$G = E - TS + PV, \tag{3.3}$$

$$F = E - TS, \tag{3.4}$$

$$H = E + PV. \tag{3.5}$$

3

在 V 不变的情况下

$$E = \int_0^T C_v(\tau)\tau\,\mathrm{d}\tau, \tag{3.6}$$

$$S = \int_0^T C_v(\tau)/\tau\,\mathrm{d}\tau. \tag{3.7}$$

$$G = \int_0^T C_v(\tau)\tau\,\mathrm{d}\tau - T\int_0^T C_v(\tau)/\tau\,\mathrm{d}\tau + PV, \tag{3.8}$$

$$F = \int_0^T C_v(\tau)\tau\,\mathrm{d}\tau - T\int_0^T C_v(\tau)/\tau\,\mathrm{d}\tau, \tag{3.9}$$

$$H = \int_0^T C_v(\tau)\tau\,\mathrm{d}\tau + PV. \tag{3.10}$$

4

一个一维简谐振子与一个温度为 τ 的热库相互作用, 简谐振子 $H = \frac{p^2}{2} + \frac{x^2}{2}$, $\tau = 1.5$(无量纲单位). 用 Metropolis 方法求相空间分布 $\rho(x, p)$.

1. 相点初始位置为 $(0, 0)$.

2. 若相点在某一点 x_1, 则在两个方向都产生一个位移, 步长为 $[0,6]$ 中的一个随机数, 到达点 x_2.
3. 根据
$$E = \mathrm{e}^{-H/\tau} \tag{4.1}$$
来计算其概率密度.
   (a) 若 $E_2 > E_1$, 则相点移动到 x_2.
   (b) 若 $E_2 < E_1$, 则产生一个 $[0,1]$ 中的随机数 ξ, 若 $\xi < \mathrm{e}^{-(H_2-H_1)/\tau}$ 则相点移动到 x_2. 否则不移动.
4. 重复 2,3, 直到给定的停止条件.

图 4.1 为散点分布图, 可以发现粒子处于原点的概率最大. 图 4.2 为二维概率密度分布图, 即 $\rho(x,p)$.

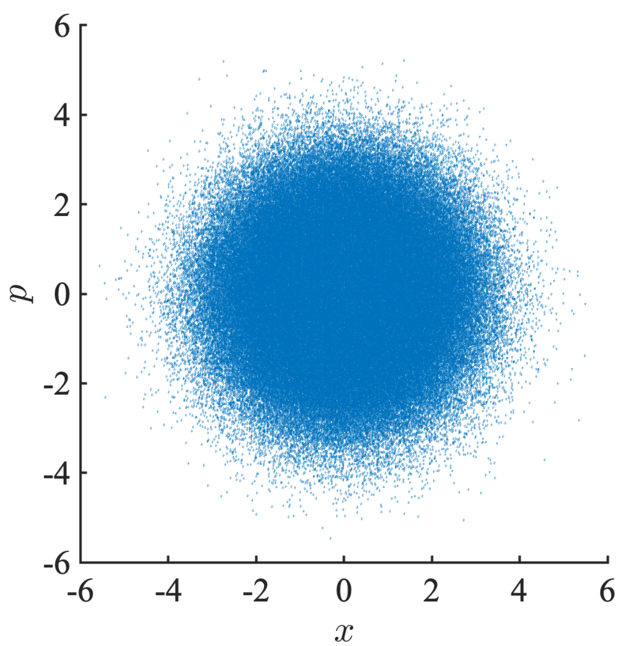

图 4.1. 散点图.

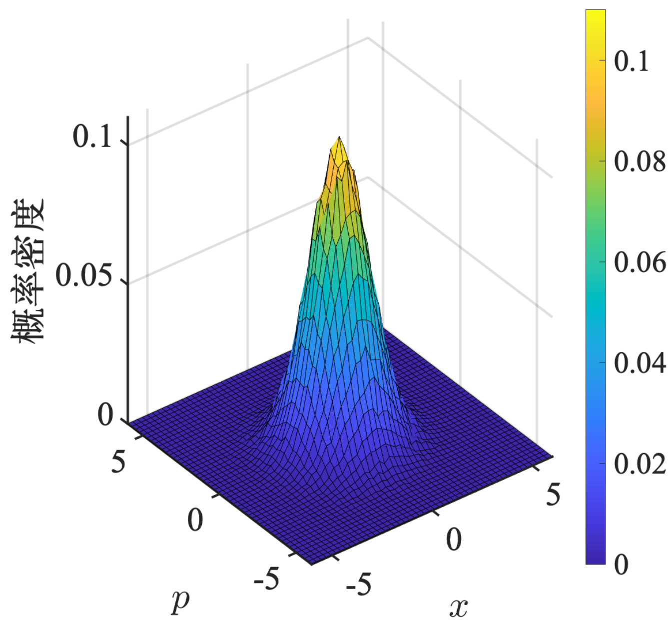

图 4.2. 概率密度图.